Metal enrichment in bauxites by deposition of chemically mature aeolian dust

George H Brimhall*, Christopher J. Lewis*, Jay J. Ague*, William E. Dietrich*, Joachim Hampel*, Tim Teague* & Peter Rix†

* Department of Geology and Geophysics, University of California at Berkeley, California 94720, USA
† Alcoa of Australia Limited, Applecross, Western Australia

Mass-balance equations applied to chemical analyses of a bauxite weathering profile in Western Australia show quantitatively that the ore-grade enrichment of aluminium is due to accumulation of aeolian dust derived elsewhere from chemically mature soils. This finding challenges the prevalent view of bauxite genesis by simple in situ *residual enrichment and suggests that regional dust trajectories may serve as a genetic link between laterites, bauxites, heavy mineral beach sands, and clay-enriched marine sediments.*

SINCE 1846, when Charles Darwin recognized the importance of atmospheric transport of land-derived dust to long-term offshore marine sedimentation[1], there has been a growing awareness of the importance of dust deflation, transport and deposition over geological timescales[2,3]. Dust deposition has been implicated in many surficial processes including evolution of landscapes in desert marginal lands[4], development of duricrusts such as calcrete layers by $CaCO_3$ influx to form caliche[5-7], loess formation[8] and significant transfer of elements from continents to the oceans[9].

Ferrugenous laterites and bauxites are widespread soils of considerable economic importance, serving both as mineable sources of Ni, Co, Al and Au and as nutrient-limited but intensively used agricultural lands[5]. For over a century, the origin of these soils has been debated, with arguments resting largely on stratigraphic, topographic and mineralogical observations. What is needed to resolve this debate, and to investigate the problem of continental weathering in general, is a means to evaluate the role in weathering profile development of dissolution, strain (volume decrease or increase), reprecipitation and vertical infiltration of detritus from external sources.

We have recently shown that a simple mass-balance approach can offer such quantitative information about the genesis of shallow supergene enrichment of Cu and Ni in laterites[10,11] and Al, Fe and Pb in podzols[11]. To test this approach in other weathering environments, we selected a well-studied, essentially 'classic' bauxite locality in the Darling Range of Western Australia[12,13] positioned along a well-known regional dust trajectory[14].

The present dust trajectories in Australia extend both westward and eastward from the arid continental interior towards adjoining Indian and Pacific Oceans. On both sides of the continent, marine sediments are dramatically enriched in kaolinite within tongues extending thousands of km offshore[14] (Fig. 1*a*). In Western Australia the trajectory of easterly winds blowing offshore is aligned with the onshore desert sand-dune trend[15]. Although the major dust trajectory is towards the west, the wind pattern affords ample opportunity for transmigration, that is, back and forth movement. In summer, strong east to west winds carry windborne dust from the desert regions of the Yilgarn Craton to the coast. In winter, on the other hand, onshore westerly winds coming from the ocean to the southwest bring the bulk of present-day rainfall and salts, which are carried well into the interior basins of southwest Australia[16] (Fig. 1*a*).

Bauxite weathering profiles are particularly useful for dust deposition analysis as their surfaces are often covered by coarse pisolites and hence may be stable to wind erosion, though much dust may blow across them with little net deflation[2]. The migratory dust path can be evaluated by determining the mineralogy of the weathering suite in each zone and ascertaining the presence of stable mineral detritus transported from external surficial deposits. Implementing this apparently simple strategy necessitates separation of chemical and mineralogical enrichments owing to several different processes: (1) residual enrichment of chemically inert species simply by *in situ* concentration during removal of more soluble mobile species, (2) enrichment due to deformation, that is volume change, and (3) actual introduction of exotic minerals, as dust from external sources, either nearby or distant. Analysis of these effects requires field description, petrographic (microscopic) examination, chemical analyses, and determination of physical properties such as density to implement, a relevant mass-balance model yielding chemical gains and losses in a well-characterized parent material[10,11].

Jarrahdale bauxite deposit

In applying our analytical techniques we have chosen a metasomatic system which, because of the homogeneity of the parent material, offers ideal opportunities for yielding unambiguous and accurate interpretation of surficial metasomatic processes. For this study, we report results from the Jarrahdale bauxite deposit in the Darling Range of Western Australia, which has developed on the Archaean Yilgarn craton consisting of gneisses, greenstones and granitic rocks (Fig. 1*b*). The weathering profile is pedogenically differentiated into five zones, which from bottom to top are: granodiorite parent material, saprolite, blocky hardcap, massive hardcap, and pisolitic gravel (Fig. 2).

Micromorphology of bauxite. Petrographic examination of hardcap samples revealed a striking geopetal fabric (Fig. 3*a*, *b*). This presents clear evidence of the introduction of fine-grained mineral grains from above and subsequent grain sedimentation in voids. Crescentic microsedimentary layers consisting largely of gibbsite, kaolinite and iron oxides occur, each with a consistent concave upward orientation similar to clay structures resulting from translocation in argillic horizons of common soils[17,18].

Continued pore-space evolution by progressive infilling and development of new voids are manifested in upward increase in the radius of curvature of microsedimentary structures within each void as well as by sedimentary unconformities produced by new void formation (Fig. 3*a*). Such features show that translocation of fine-grained mineral grains is a dominant feature of the fabric of the hardcaps. This being so, one must ask how much of the aluminium and iron enrichment so characteristic of bauxites in general is due to influx of ferruginous and aluminous minerals from external sources.

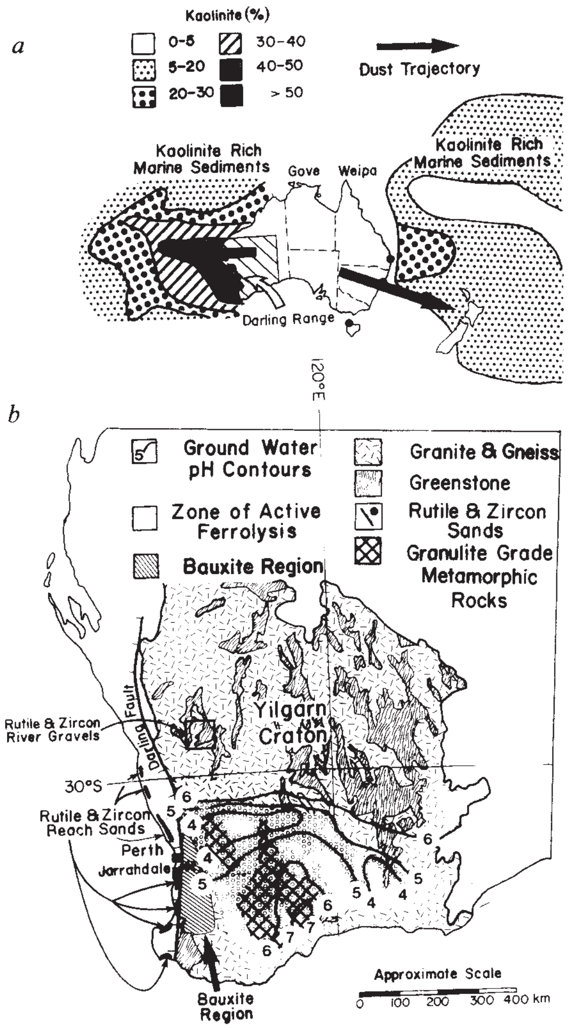

Fig. 1 *a*, Westward and eastward dust trajectories extending from the arid interior of Australia to the Indian and Pacific Oceans (from Pye[2] and Windom[14]). Katolinite-rich marine sediments extend along the dust trajectories. Shoreline heavy-mineral beach deposits are shown as black dots. *b*, Location of the Jarrahdale bauxite deposit in the Darling Range of Western Australia adjacent the Darling Range Fault. The sampling locality is the same deep railroad cutting as studied in detail by Sadleir and Gilkes[21] and compared with other world-class bauxite deposits elsewhere in northern Australia at Weipa and Gove[13]. Regions of active ferrolysis and surficial heavy-metal remobilization occur immediately east of the bauxites where acid saline lakes and groundwater are prevalent[20]. Granulite terrains are from Vallance[21].

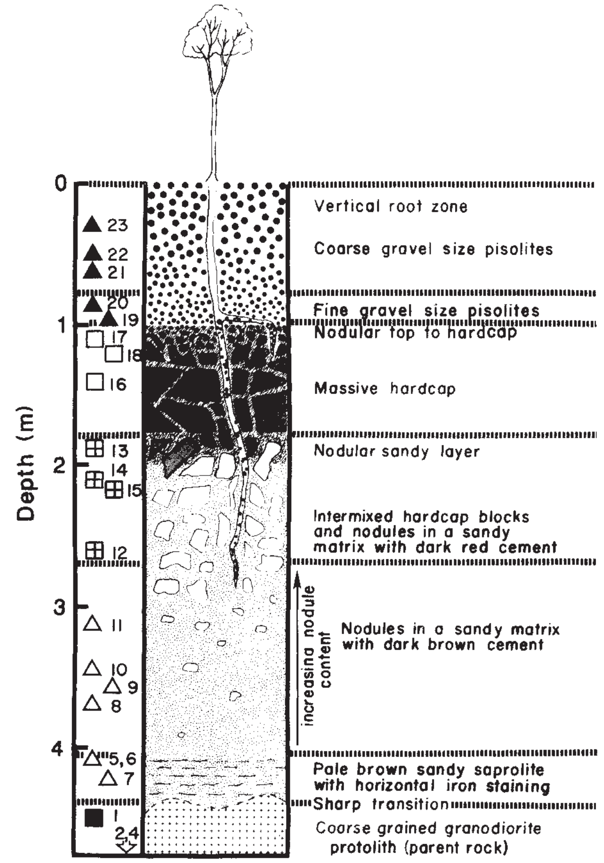

Fig. 2 Weathering profile in exposed railroad cutting through Craiges Ridge, 0.7 km southwest of the Alcoa no. 2 mine site. A total of 23 samples (1129-1 to 1129-23) were taken as shown. Symbols represent sample type: bedrock (■), saprolites (△), hardcap (□) and pisolites (▲). Quantitative modal petrography of the granite protolith (samples 1-4) was determined by computer-assisted line integration with a digitizing microscope[19]. The average mode of the granodiorite consists of 52% plagioclase, 32% quartz, 10% microline and 3% biotite. The remaining 3% consists of the igneous accessory minerals, sphene, magnetite, apatite and zircon and alteration epidote, calcite and chlorite in decreasing order of abundance. No rutile or anatase was identified. The overlying saprolite becomes progressively richer in nodules and blocks of hardcap in its upper portions. Above the hardcaps, pisolites become progressively coarser upwards. Bedrock and hardcap were sampled by hammer and chisel while soils were samples with a hand-held piston coring device from which undistributed soil cores 48 mm in diameter and 77 mm in length were taken and recovered inside durable plastic tubes. During soil sampling no compression of the soils was observed, so that subsequent density measurements are representative of the in-place soils.

Chemical and mechanical processes

A chemically immobile element must be identified with which to gauge the gains and losses of other, more mechanically and chemically mobile elements, and with which to calculate strain[11]. In these bauxites there are two possibilities: Zr and Ti. We find, however, that as well as being residually concentrated, both of these elements have themselves been introduced into the profile as zircon and rutile. As key stable minerals, the extent of Zr and Ti enrichment by introduction must be determined before introduction of other elements can be studied.

Depth of zircon and rutile translocation. We prepared concentrates of zircon and rutile from each sample by dissolving away more abundant minerals with a weak HF and aqua regia leach solution. By leaching samples without crushing, we retained the original size and morphology of these accessory minerals, which were resistant to acid attack. Rutile grains were invariably highly rounded and restricted to a near-surface zone extending from the pisolites down through the blocky hardcap (Fig. 4*a*). No rutile was present in the parent granodiorite. The mean diameter, maximum diameter and abundance of rutile grains decreased consistently with depth as determined with the digitizing microscope[19].

Two populations of zircon occur: colourless, well-rounded grains occurring only in the pisolitic zone, and cloudy, perfectly euhedral and zoned grains ubiquitous in the profile and clearly derived from weathering of the granodiorite. The average zircon grain diameter decreased with depth to the base of the hardcap, but then abruptly increased in the upper saprolite to a stable value similar to that of the granodiorite (Fig. 4*b*). We interpret the rutile and zircon grain size, morphology and abundance profiles above the base of the hardcap as resulting principally from translocation of rounded rutile and zircon downward from the surface.

Pore size restrictions: a porous media sieve. By determining the average pore diameter in stained epoxy-impregnated thin sections we have shown that pore diameter decreases with depth (Fig. 4*c*). The depth of translocation is therefore governed by the relative sizes of translocated grains and the diameter, shape and tortuosity of pore structures encountered during passage through the bauxite. We conclude that rutile and zircon translocation is limited by pore size, which in turn is controlled by the extent of pore infilling by Al and Fe compounds and continued void formation by eucalyptus tree roots. The bauxite profile has clearly behaved as a porous media sieve that tends to trap infiltrating exotic and neoformed mineral grains, producing a grain-size sorting effect.

Separation of fractionation processes

Here, p stands for properties of the parent material or protolith, residual increase in concentration of chemically immobile elements, (2) internal collapse or strain, and (3) translocation of exotic grains can each be quantitatively assessed[10,11]. Zr is determined by X-ray fluorescence and other metals investigated were determined by flame or flameless atomic absorption spectroscopy.

Residual enrichment. Using constitutive mass-balance equations relating chemical concentration to density and volume of weathering zones, we have demonstrated previously[10,11] the utility of expressing metasomatic changes in terms of the ratio of the concentration of a given element (i) in a weathered sample ($C_{i,w}$) to the concentration in the parent material ($C_{i,p}$). This unitless fractionation factor, $C_{i,w}/C_{i,p}$, is greater than unity for enrichment, or less than unity for depletion of an element, i. These fractionation factors for the two most important elements in bauxite, Fe and Al, are shown in Fig. 5. We have shown that in the absence of deformation and translocation effects, the enrichment factor due to simple residual concentration is a simple function of density[11]:

$$C_{i,w}/C_{i,p} = \rho_p/\rho_w \tag{1}$$

Here, p stands for properties of the parent material or protolith, w for properties of the weathered material, and ρ is bulk density. Figure 5 shows the overall enrichment factor for each sample with a symbol for each depth zone. The component of the overall enrichment factor due to simple residual enrichment, given by equation (1), is shown with a dashed line and accounts for only a small fraction of the overall Fe and Al concentration, indicating that translocation and strain must be important.

Volumetric change (strain). Strain due to weathering, $\varepsilon_{i,w}$, is defined here in one dimension as the change in length divided by the original length. If the vertical dimension of a representative volume of protolith before weathering is B_p and after weathering is B_w, the strain $\varepsilon_{i,w}$ is simply $(B_{i,w} - B_{i,p})/B_{i,p}$. In addition it can be shown[11] that strain can be related to the fractionation factor:

$$\frac{C_{i,w}}{C_{i,p}} = \frac{\rho_p}{\rho_w}\left(\frac{1}{\varepsilon_{i,w}+1}\right) \tag{2}$$

We determine the amount of chemical enrichment due to strain by first applying our measurements on the depth of heavy mineral translocation. Below this depth, any enrichment of Ti and Zr in excess of residual enrichment is due to deformation, as no evidence of dissolution or reprecipitation of rutile or zircon exists.

The net strain due to weathering, $\varepsilon_{i,w}$, is determined from equation (2), which is a complete closed-system form of equation (1).

Combined residual enrichment and strain. Figure 5 shows the component of the overall enrichment factor (data points) accounted for by strain and residual enrichment, using a solid line based on equation (2). This function approximates the whole-rock data much more closely than residual enrichment alone (dashed line). But near the top of the profile, even this combined function accounts for only a small part of the overall enrichment; the remainder is due to open-system enrichment.

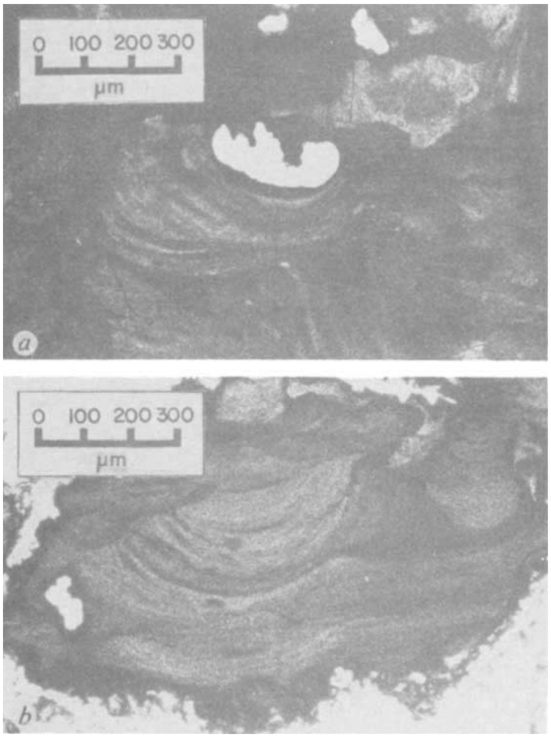

Fig. 3 Micromorphological features of blocky hardcap sample (1129-12) shown in plane polarized light. All massive and blocky hardcap samples of the bauxite profile were impregnated with blue-coloured epoxy under vacuum in order to prepare thin (30 μm) and ultra-thin (5 μm) sections so that delicate pore structures were preserved and could be measured. Partly (*a*) and completely (*b*) infilled pores with crescentic microclastic deposits (films) of gibbsite, kaolinite and iron oxides filling voids within blocky hardcap (sample 1129-12). The radius of curvature of geopetal infillings increases as pores decrease in size. A microsedimentary unconformity is apparent in the lower right-hand side of (*a*).

Open-system transport (τ). To measure the addition or extraction of material either by translocation or solute migration, equation (2) can be expanded to

$$\frac{C_{i,w}}{C_{i,p}} = \overset{\text{closed system}\atop (1)}{\frac{\rho_p}{\rho_w}\left(\frac{1}{\varepsilon_{i,w}+1}\right)} + \overset{\text{open system}\atop (2)}{\frac{100\, m_{i,\text{influx}}}{C_{i,p}\rho_w B_w}} \tag{3}$$

where $m_{i,\text{influx}}$ is the mass of element i, added to an elementary volume of vertical dimension B_w.

Translocation. Solving equation (3) for the mass influx, $m_{i,\text{influx}}$, and dividing by the mass of element i contained initially in the original parent interval, $C_{i,p}\rho B_p$, yields

$$\tau_{i,w} \equiv \frac{100\, m_{i,\text{influx}}}{C_{i,p}\rho_p B_p} = \frac{\rho_w}{\rho_p}\frac{C_{i,w}}{C_{i,p}}(\varepsilon_{i,w}+1) - 1 \tag{4}$$

where $\tau_{i,w}$ is mass added to the unweathered closed system, which is zero when there has been no translocation. If τ is positive, an influx of material has occurred: if τ has a value of +5, for example, translocation accounts for five times or 500% the mass of element i, contained in the unweathered material. If τ is negative, material has left the system in suspension. The minimum possible value of τ is −1.0 or −100% for total depletion. The utility of the transport function, τ, is in recognizing regions within the weathering profiles where elements have been

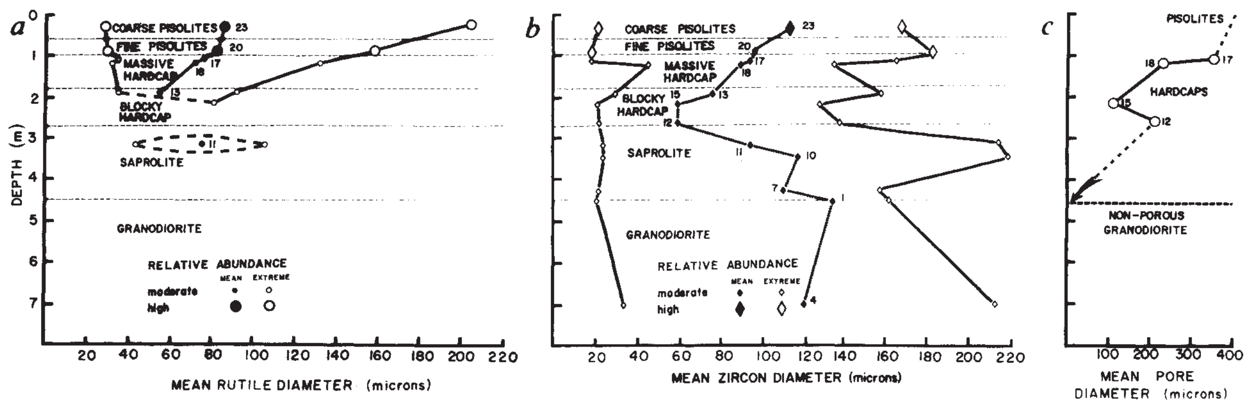

Fig. 4 *a*, Distribution, relative abundance and size range of rutile with depth in the weathering profile. The average and maximum grain size of rutile decreases with depth. Rutile is present only above the saprolite and is a transported, exotic mineral. *b*, Distribution, abundance and size range of zircon. The average grain size of zircon decreases to a depth of 2.5 m, below which the fine-grained, rounded and abraided exotic variety no longer persists. *c*, Average diameter of pores in the hardcaps. There is an overall decrease from very large macropores in the pisolitic zone to an absence of even μm-signal pores in the granodiorite bedrock.

added or removed (Fig. 5). The pore fillings in the bauxite hardcaps suggest that mass influx occurs by translocation of mineral particles rather than reprecipitation of solutes in solution, although microchemical precipitates occur as void infillings (Fig. 3*a*). Near the top of the profile both Fe and Al have been added to the system, whereas near the saprolite-bedrock interface small amounts of these elements have been removed. One of the highest observed values of τ is ~1,000% for Fe, indicating that for each gram of Fe in the parent material 10 g has accumulated. For Al, τ approaches 300%, showing that residual enrichment accounts for only a very small fraction of the Al in the profile. Most is added by translocation by Al-rich detrital minerals formed by chemical weathering elsewhere. But as the new transport function, τ, is not indicative of the distance of transport before influx of grains into the profile, the material could be entirely allochthonous or, if derived more locally, parautochthonous, or both. Figure 6 shows that a suite of other elements have similarly been systematically introduced into the top of the profile. This suite included Zr, Ti, V, Cr and Mo. None of these elements have local source regions ($\tau = 0$) within the profile.

External source of heavy metals

The particular suite of introduced metals (Fe, Al, Zr, Ti, Cr and Mo) in combination with the lack of any evidence of quartz enrichment (τ for Si is slightly negative, consistent with retention of primary quartz) is indicative of a source material peculiarly enriched in these elements and surprisingly deficient in quartz. This enigma is resolved by considering specific surficial processes and bedrocks in the region immediately east (upwind) of the bauxite studied (Fig. 1*b*). Here hydrogeochemical zoning patterns in the Yilgarn block have developed by shallow redistribution of elements during weathering, including concentration of Fe, Pb, U and Au[20].

Saline seepages, salt lakes and playa systems span >80% of this region. High concentrations of Fe and Al have been recognized in acid saline groundwaters with $pH < 4$ through ferrolysis, a process by which Fe^{2+} is oxidized to Fe^{3+} above the groundwater table and precipitated as iron oxide with the liberation of H^+ (ref. 20):

$$4Fe^{2+} + 6H_2O + O_2 = 4FeOOH + 8H^+ \qquad (4)$$

The region of active ferrolysis is characterized by heavy-metal remobilization, particularly those metals whose solution chemistry is controlled by a change in oxidation state[20]. We hypothesize that the regional source of the transported heavy-metal suite contaminating the upper portions of Jarrahdale bauxite profile are surficial laterite and ferricretes, deficient in quartz but enriched in rutile and zircon and metals due to intense ferrolysis in Western Australia. The occurrence of granulite grade[21] metamorphic rocks (Fig. 1b) containing orthopyroxene, which is exceptionally susceptible to rapid low-temperature oxidation to haematite and kaolinite[22], suggests that regional lithological factors may also contribute to ferrolysis (R. C. Newton, personal communication). The metallic elements, concentrated near the surface, may be transported as complex dust and detrital primary minerals in the aeolian dust. Elsewhere, for example in Nigeria, iron-oxide-rich dust blown southward from the Sahara Desert has been implicated as a major additive in soils[23]. Although aluminous weathering products such as gibbsite and kaolinite are unquestionably developed *in situ* by hydrolysis reactions of feldspar, and chemically resistant heavy minerals such as zircon are residually enriched as well, major addition of detrital phases has occurred and dominates the chemistry of the top the Jarrahdale bauxite profile. The high porosity and pore structure of bauxites are ideal for translocation and are developed through continued pedoturbation by tree

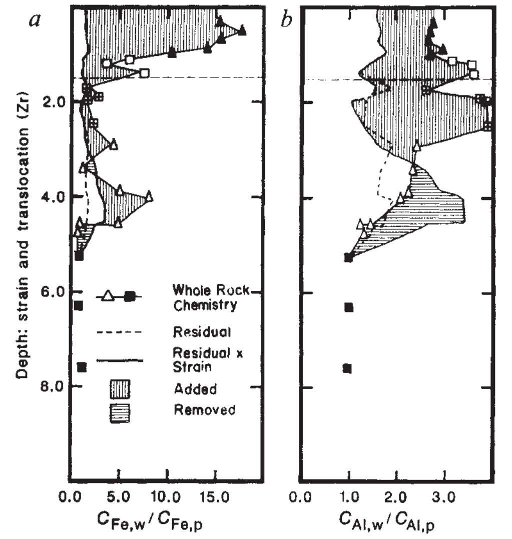

Fig. 5 Contributions of residual enrichment, strain and translocation to enrichment of Fe (*a*) and Al (*b*) using Zr for strain determination. Symbols indicate the horizons shown in Fig. 2. Residual enrichment, represented by the dashed line, is simple ρ_p/ρ_w. Most of the Fe and Al is introduced into the profile from above. Depths shown are corrected for collapse. Zones where Zr translocation has been demonstrated are assumed to have experienced no strain.

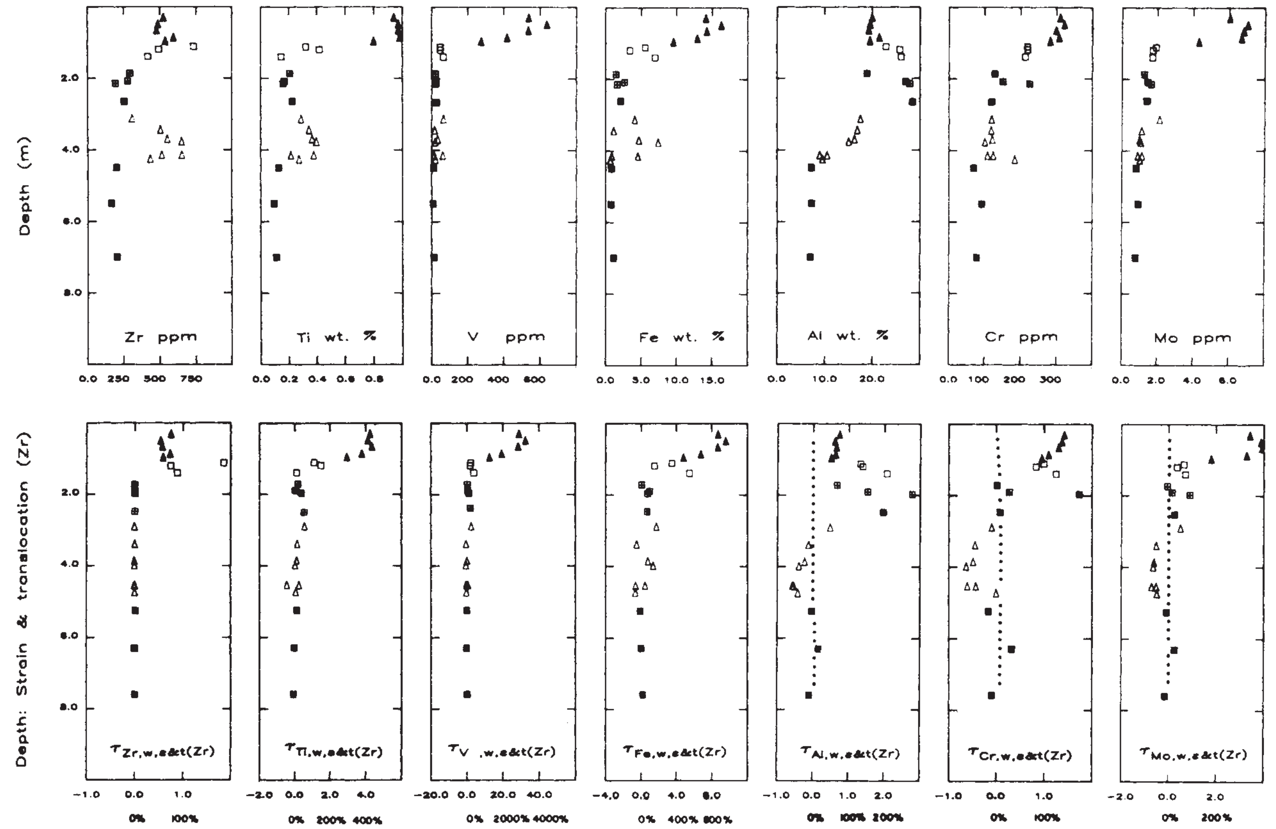

Fig. 6 Variation in mechanical transport function, τ, with undeformed depth for Zr, Ti, V, Fe, Al, Cr and Mo, using Zr to calculate strain. Effects of residual and deformational enrichment are taken into account. Vertical dotted line indicates zero translocation. Positive values of τ indicate addition to the profile; negative values, subtraction. All of these elements have been added to the top of the profile. Al, Cr and Mo have also been slightly removed from the bottom of the profile.

roots forming a network of channels and tubular voids which provide access for surficial grains to the subsurface[24]. The replacement of lithostructure by pedostructure occurs through infilling of voids with exotic sediment.

Dust deposition. During weathering, continued partial erosion of bauxite and laterite profiles supplies a pre-enriched material for subsequent transport and recycling of these stable and resistant mineral species to adjacent regions to the west. The resultant chemical enrichment is in fact largely mechanical at the site of deposition. Besides weak residual and volumetric enrichment, fractionation occurs by translocation and porous media sieving, as grain-size sorting is affected by progressive impedance of grains by pore restrictions. The exotic material added to bauxites are mature detrital grains that have been released from their previous surficial position. Hence they are largely unreactive within their new environment and may persist indefinitely without modification until later released by abrasion or erosion. We therefore view bauxite genesis as a continuing cumulative fractionation process involving dust migration, with eclectic grain mixtures developing along the dust trajectory by temporary storage in the shallow subsurface. Although cumulative soil formation involving addition of detrital parent material during weathering is not a new idea[18,24,25], for instance allochthonous karst bauxite development on limestones in the Mediterranean[26,27], this is the first conclusive proof that addition of aeolian material perhaps in combination with parautochthous enrichment products can be a major factor in the genesis of true bauxites occurring along a regional dust trajectory.

Mineralogical anomalies. With this conclusion we can reconcile mineralogical anomalies previously recognized by Grubb[28] with the simple residual bauxitization of granitic bedrock proposed earlier[24,29-33] by *in situ* transformation involving extreme fractionation by chemical selectivity[34]. Within the upper portions of numerous profiles in the Darling Range a distinctive, abraded heavy-mineral suite consisting of zircon, rutile and ilmenite, each of several varieties, was interpreted by Grubb[28] to be largely exotic in origin as many laterites contained components not found in the bedrock. Grubb attributed this detrital suite to residual weathering of a composite parent material consisting of a coarse feldspathic fluviatile mantle of sediments inferred to have once overlain the Archaean granite bedrock. Sadleir and Gilkes[12] criticized this hypothesis, and demonstrated that bauxite mineralogy varied with underlying bedrock lithology of gneisses and basaltic dikes. They also cited the absence of any fresh rock at the base of the profiles Grubb[28] studied as being another deficiency in his interpretation. They consequently concluded that the bauxite was a residual product of weathering, but they failed to resolve the origin of the abraded heavy-mineral suite. Glassford and Killigrew[35] argued that desert conditions once existed throughout the southwest of Australia. Davy[36] concluded subsequently that windblown minerals would therefore be expected over this expansive region, but stated that the origins of the exotic accessory minerals and the means of their incorporation into the caprock had not been clearly identified. We show that the only weathering process consistent with interpretation of the new chemical, physical and microtextural data is that, rather than derivation from the inferred sedimentary mantle for which there is little geological evidence, the abraded mineral suite and, surprisingly, the major portion of the Al and Fe were introduced into the top of the bauxite profiles by widespread aeolian activity (Fig. 1*a*). Unlike local residual enrichment, which we show to be a minor factor, translocation of minerals of either allochthonous or parautochthonous origin can produce large detrital enrichment factors not only for accessory minerals but also for major ore-forming minerals such as kaolinite and gibbsite.

Association of bauxites and heavy-mineral beach sands. As kaolinite is only one of the characteristic secondary minerals enriched by intense chemical weathering, chemically resistant primary mineral grains concentrated by chemical weathering must similarly be transported westwards from the continental interior, though not necessarily the same distance as kaolinite. If the entire mixed-weathering mineral suite consisting of stable, chemically mature minerals becomes airborne, then the denser, coarser detritus may be deposited onshore in a closer subaerial environment than the offshore accumulation of kaolinite (Fig. 1*a*). We base this inference on the surficial deposits observed along the dust trajectory, each of which contains both primary and secondary mineral grains that are relatively stable with respect to chemical weathering. The east-west sequence (Fig. 1*b*) consists of laterite and ferricrete duricrust regions within closed acid saline basins[20,37-39], nearby proximal bauxite deposits in the Darling Range[12,13], shoreline beach deposits enriched in detrital heavy minerals including zircon and rutile[40-42], and finally distal offshore submarine pelagic sediments enriched in kaolinite[14]. We postulate that the surficial deposits in this sequence are genetically related and result from progressive mechanical fractionation and selective deposition of the aeolian mineral population. Because of their high porosity the upper portions of bauxite and laterite weathering profiles along the trajectory may be temporary, though long-lived, repositories for airborne dust derived from source regions toward the east, therefore offering practical means of sampling long-term dust deposits. This conclusion leads us to look globally at the distribution of large bauxite and laterite deposits occurring at tectonically stable continental margins (Australia, Ghana, Guinea and Sierra Leone in West Africa and India) where world-class heavy-mineral (rutile, zircon, monazite) shoreline deposits occur[41-44], and to infer that major offshore dust trajectories, in combination with fluviatile systems, control migration paths and fractionation of mature mineral suites on their long-term passage to the sea. Efficient cumulative enrichment involving continental weathering occurs by a combination of stripping apparently older surficial debris, its aeolian transport, and entrapment in more humid coastal environments after derivation from an almost infinite source region undergoing aridification.

We thank Roger Vines and Shane Sadleir for assistance with the field work, which was coordinated by Roy Woodal; we also thank Oliver Chadwick, Graham Reynolds, Peter Ball, Charles Gilbert, Hans Jenny, Kathy Danti and Shari Shute for discussions and assistance.

Received 21 December 1987; accepted 22 April 1988.

1. Darwin, C. *Q. geol. Soc. Lond.* **2,** 26-30 (1846).
2. Pye, K. *Aeolian Dust and Dust Deposits* (Academic, London, 1987).
3. Pewe, T. L., Pewe, E. A., Journaux, A. & Slatt, R. M. *Spec Pap. geol. Soc. Am.* **186,** 169-190 (1981).
4. McTainsh, G. H. & Pitblado, J. R. *Earth Surf. Process Landforms* **12,** 415-424 (1987).
5. Coque, R. *Ann. Geog.* **64,** 359-370 (1955).
6. Goudie, A. S. *Duricrusts* (Clarendon, Oxford, 1973).
7. Watson, A. *Sedimentology* **32,** 855-876 (1985).
8. Richthofen, F. von *Geol. Mag.* **9,** 293-305 (1882).
9. Goldberg, E. D. *Comments Earth Sci Geophys.* **1,** 117-196 (1971).
10. Brimhall, G. H., Alpers, C. & Cunningham, A. B. *Econ. Geol.* **80,** 1227-1254 (1985).
11. Brimhall, G. H. & Dietrich, W. A. *Geochim. cosmochim. Acta* **51,** 567-587 (1987).
12. Sadleir, S. B. & Gilkes, R. J. *J. geol. Soc. Aust.* **23,** 333-344 (1976).
13. Loughnan, F. C. & Sadleir, S. B. in *Bauxite* (ed. Jacob, L.) 436-450 (Am. Inst. Metallurg. Petrol. Engrs, New York, 1984).
14. Windom, H. L. *J. Sedim. Petr.* **45,** 520-529 (1975).
15. Brookfield, M. *Z. Geomorph. Suppl.* **10,** 121-158 (1970).
16. Hingston, F. & Gailitis, V. *Aust. J. Soil Res.* **14,** 319-335 (1976).
17. McKeague, J. A. in *Soil Micromorphology* (eds Bullock, P. & Murphy, C. P.) 369-371 (Academic, Berkhamsted, 1981).
18. Birkeland, P. W. *Pedology, Weathering and Geomorphological Research*, 146-147 (Oxford University Press, New York, 1974).
19. Brimhall, G. H. & Rivers, M. L. *United States Patent* 4, 503, 555 (1985).
20. Mann, A. W. in *Geochemical Exploration in Deeply Weathered Terrain* (ed. Smih, R. E.) 158-167 (CSIRO Inst Energy and Earth Resources, Wembley, 1983).
21. Vallance, T. G. *Metamorphic Map of Australia* (Bureau of Mineral Resources, Sydney, 1983).
22. Janardhan, A. S., Newton, R. C. & Hansen, E. C. *Contr. Miner. Petr.* **79,** 130-149 (1982).
23. Vine, H. *Tech. Commun. Commonwlth Bur. Soil Sci.* **46,** 22-29 (1949).
24. Tardy, Y. & Nahon, D. *Am. J. Sci.* **285,** 865-903 (1985).
25. Nikiforoff, C. C. *Soil Sci.* **67,** 219-230 (1949).
26. Vadász, E. *Bauxitföldtan* (Akademiai Kiado, Budapest, 1951).
27. Valeton, I. *Bauxites*, 145-147 (Elsevier, Amsterdam, 1972).
28. Grubb, P. L. C. *Econ. Geol.* **66,** 1005-1016 (1971).
29. Baker, G. F. U. *Bull. Bur. Miner. Resourc. Geol. Geophys. Aust.* no. 141, 223-224 (1973).
30. Geidans, L. *Australas, Inst. Min. Metall. Conf. Perth* **3,** 173-182 (1973).
31. Hutton, J. T. *Divl Rep. Div. Soils CSIRO* **11,** 55-56 (1955).
32. Tomich, S A. *Proc. Australas. Inst. Min. Metall.* **212,** 125-135 (1965).
33. Valeton, I. in *Lateritisation Processes* (Proc. Int. Seminar on Lateritisation Processes) 15-23 (Balkem, Rotterdam, 1981).
34. Norton, S. A. *Econ. Geol.* **68,** 353-361 (1973).
35. Glassford, D. K. & Killigrew, L. P. *Search* **7,** 394-396 (1976).
36. Davy, R. *Geol. Surv. Western Aust.*, Report 8 (1979).
37. Mann, A. W. *Econ. Geol.* **79,** 38-49 (1984).
38. Mann, A. W. & Ollier, C. D. *Catena Suppl.* **6,** 152-157 (1985).
39. Webster, J. G. & Mann, A. W. *J. Geochem. Explor.* **22,** 21-42 (1984).
40. Fantel, R. J., Buckingham, D. A. & Sullivan, D. E. *Informn Circ. U.S. Bur. Mines.* **9061**.
41. Baxter, J. L. *West Austr. Geol. Surv. Min. Resourc. Bull.* **10** (1977).
42. Baxter, J. L. in *Australia: A World Source of Ilmenite, Rutile, Monazite and Zircon*, 1-8 (*Australian Institute of Mineral Metallurgy, Victoria*, 1986).
43. Derry, D. R. *World Atlas of Geology and Mineral Deposits* (Mining Journal Books, London, 1980).
44. Dixon, C. J. *Atlas of Economic Mineral Deposits* (Cornell, Press, New York, 1979).

DNA sequence determinants of CAP-induced bending and protein binding affinity

Marc R. Gartenberg and Donald M. Crothers

Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA

The sites of DNA bending induced by binding catabolite activator protein are identified and shown to coincide with positions where DNA grooves face the protein. The bendability of DNA with different sequences at these bend centres parallels the bending preference of the sequences in nucleosomal DNA. Anisotropic DNA bendability significantly affects the structure and strength of regulatory protein-DNA complexes.

ELECTROPHORETIC analysis has revealed that the catabolite activator protein (CAP) bends its DNA binding site in the *Escherichia coli lac* promoter[1-3]. The accelerated cyclization kinetics of CAP-bound fragments[4,5], hydrodynamic properties of CAP-DNA complexes[6] and models based on the protein's crystal structure[7,8] support this interpretation. Now protein-induced DNA bending is recognized as a structural motif common to many protein-DNA complexes[9-17]. The structural requirements governing protein-induced bends are not fully understood; however, electrophoretic characterization of several mutant *lac* promoter-CAP complexes has demonstrated that DNA sequence determinants within the protein binding site modulate the extent of protein-induced bending. The L8 consensus mutation[1], the right-hand symmetrized binding site[18], and sequence changes outside the central 28 base pairs (bp)[18] reduce the overall bend.