

aerospace and automotive industries. In solid oxide fuel cells, the addition of Sc to the electrolyte improves conductivity and lowers the operating temperature, extending fuel cell life.

Despite a crustal abundance of *ca.* 22 ppm (Rudnick and Gao, 2014), comparable to common elements such as copper or lead, current Sc production is limited to 10 t to 15 t per year (U.S. Geological Survey, 2016). The large ratio of ionic radius to charge of Sc^{3+} hinders the concentration of scandium during most geochemical processes (Samson and Chassé, 2016). A notable exception concerns lateritic deposits developed over ultramafic–mafic rocks where Sc concentrations up to 100 ppm make it a potential by-product (Aiglsperger *et al.*, 2016; Maulana *et al.*, 2016). Recently, lateritic deposits with Sc concentrations high enough to mine as a primary product have been reported in Eastern Australia (Jaireth *et al.*, 2014). Among these, the Syerston–Flemington deposit contains about 1350 t of Sc at an average concentration of 434 ppm Sc (Pursell, 2016), providing a century-long resource at the present levels of world consumption.

We present the first data on Sc speciation in lateritic deposits by combining quantitative mineralogy, geochemical analysis and X-ray absorption near-edge structure (XANES) spectroscopy on drill-core samples from the lateritic profile of the Syerston–Flemington deposit. The results explain the geochemical conditions required to form such exceptional Sc concentrations and improve our understanding of the geochemical behaviour of this under-explored element.

Geological Context

In Eastern Australia, lateritic profiles developed under seasonally dry humid tropical climatic conditions that resulted in intensive weathering during the Tertiary; the present occurrences are often erosional remnants of fossil laterite (Milnes *et al.*, 1987). The Syerston–Flemington deposit (Fig. 1a and Table S-1) is part of the lateritic cover developed over the Tout complex, an ultramafic–mafic ‘Alaskan-type’ intrusive complex in the Lachlan Fold Belt (Johan *et al.*, 1989). Scandium anomalies have been found over a body of nearly pure clinopyroxenite (Fig. S-1), with Sc concentrations (*ca.* 80 ppm; Table S-3) twice as high as those in typical mantle clinopyroxenites (Samson and Chassé, 2016). Similar concentrations (60 ppm to 80 ppm) occur in other ‘Alaskan-type’ clinopyroxenites (Burg *et al.*, 2009) and in clinopyroxenes from ocean-island basalts (Dorais, 2015). This suggests the accumulation of clinopyroxene in subvolcanic feeder conduits during fractional crystallisation of a mantle-derived melt. Anomalies of Sc concentration in the parent rock result from specific conditions of formation and are not shared by all ultramafic–mafic bedrocks.

Scandium speciation in a world-class lateritic deposit

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Abstract

Scandium (Sc) has unique properties, highly valued for many applications. Future supply is expected to rely on unusually high-grade (up to 1000 ppm) lateritic Sc ores discovered in Eastern Australia. To understand the origin of such exceptional concentrations, we investigated Sc speciation in one of these deposits. The major factors are unusually high concentrations in the parent rock together with lateritic weathering over long time scales in a stable tectonic context. At microscopic and atomic scales, by combining X-ray absorption near-edge structure spectroscopy, X-ray diffraction and microscopic and chemical analyses, we show that Sc-rich volumes are associated with iron oxides. In particular, Sc adsorbed on goethite accounts for *ca.* 80 % of the Sc budget in our samples. The remaining Sc is incorporated in the crystal structure of haematite, substituting for Fe^{3+} . Scandium grades reflect the high capacity of goethite to adsorb this element. In contrast, the influence of haematite is limited by the low levels of Sc that its structure can incorporate. These crystal-chemical controls play a major role in lateritic Sc deposits developed over ultramafic–mafic rocks.

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Introduction

Scandium is embedded in the very fabric of modern society, making it one of the most valuable elements. End-uses range from biomedical research to electronics, lasers and ceramics but the demand is driven by energy issues (Emsley, 2014). Scandium finds applications in Al–Sc superalloys, increasing tensile strength and improving weldability while maintaining light weight, an energy-saving factor in

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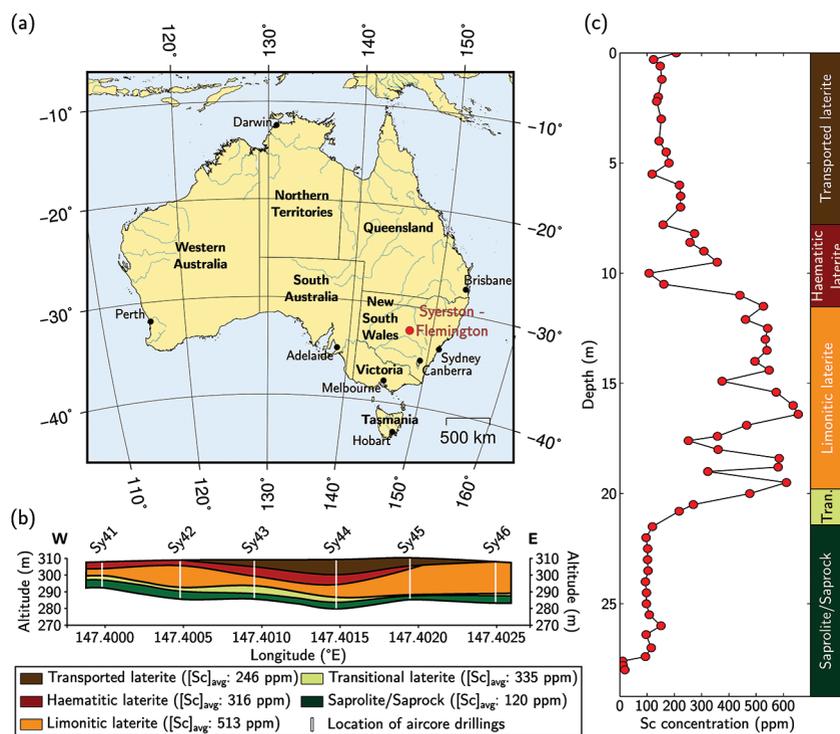


Figure 1 (a) Geographical location of the Syerston–Flemington deposit. (b) Schematic cross section of the lateritic cover forming the Syerston–Flemington deposit, constructed from petrographic analysis of drill-cores. Average Sc concentrations ($[Sc]_{avg}$) are calculated for each layer from ICP-MS analyses of samples collected every metre on each core. (c) Distribution of Sc with depth along the different levels of a typical profile (Tran.: transitional laterite).

Core Sampling and Analytical Methods

Each metre of 26 vertical aircore holes has been analysed for Sc and two diamond drill-cores of about 30 m length have been sampled to collect rock chips from the limonitic part of the lateritic cover. Quantitative mineralogical compositions were determined by X-ray diffraction (XRD) and Rietveld refinement. Major and trace elements were determined by X-ray fluorescence (XRF) analysis and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Mapping of major elements was done using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDXS) on polished sections of samples embedded in epoxy resin. The electron microprobe (EMP) gave point analyses for major and minor elements along with Sc. The distribution of Sc was mapped by synchrotron

micro-X-ray fluorescence (μ -XRF). Scandium speciation was determined by synchrotron-based micro-X-ray absorption near-edge structure (μ -XANES) spectroscopy at Sc and Fe K-edges. Detailed descriptions are given in the Supplementary Information.

Characteristics of the Lateritic Deposit

The lateritic profile shows five levels (Fig. 1b; see also Supplementary Information, Section 2 and Table S-2); from bottom to top: saprolite, with smectite from the weathering of clinopyroxene, which is still visible in the deepest parts; transitional laterite where smectite is progressively replaced by Fe oxides and kaolinite; limonitic laterite dominated by goethite with haematite, kaolinite and gibbsite; haematitic laterite dominated by haematite with goethite, kaolinite and gibbsite; and transported laterite of similar composition but containing clasts and evidence of former alluvial channels. Similar lateritic profiles are developed over other ultramafic–mafic rocks in Australia (Anand and Paine, 2002), with most of the weathering profile directly inherited from the parent rock except for the transported level. The depth of the profile indicates that the weathering occurred over long time scales, possibly starting as early as 430 million years ago (Fergusson, 2010), in a stable tectonic context. Bulk assays show that Sc concentration increases upward, from ca. 100 ppm in the transitional laterite to ca. 500 ppm in the limonitic laterite (Fig. 1b,c and Table S-3). The concentration then decreases in the haematitic laterite and drops to ca. 250 ppm in the transported laterite.

Identification of Iron Oxides as Main Scandium Hosts

The mineralogy is typical of lateritic profiles developed over ultramafic rocks (Freyssinet *et al.* (2005); Fig. 2a,b and Table S-4). The ore is dominated by haematite and Al-bearing goethite, associated with kaolinite and gibbsite. Minor phases include anatase, quartz and an Fe oxide with an inverse spinel structure, either maghemite or magnetite. The broad X-ray diffraction lines (Fig. 2a) reflect the poor crystallinity or small particle size (<100 nm) of the Fe oxides. The bulk Sc content is correlated with the proportion of Al-bearing goethite, indicating its potential role as a Sc host in the ore (Fig. 2c).

Systematic SEM–EDXS mapping confirms the absence of discrete Sc phases, as expected from the scarcity of such phases in nature (Samson and Chassé, 2016). The EMP analyses of Si, Ti, Al, Fe and Sc have been averaged on each grain type, as identified by combining SEM images, major elements and Sc contents and applying statistical clustering (Supplementary Information, Section 6 and Table S-6). Scandium contents are low to extremely low in Al-rich grains (ca. 300 ppm), Ti-rich oxides (ca. 100 ppm) and quartz (below detection limit, ca. 30 ppm). The highest Sc contents (ca. 1300 ppm) are encountered in Fe



oxide grains that contain Al (*ca.* 7 wt. %) and have low EMP analytical totals (*ca.* 85 wt. %). These grains appear to correspond to the Al-bearing goethite identified by XRD. Another type of Fe oxide grains, with a lower concentration of Sc (*ca.* 200 ppm) and high Fe could correspond to the haematite phase identified using XRD.

Much of each sample consists of a fine-grained matrix with three distinct compositions. Two correspond to mixtures of Fe oxides with different Sc contents, *ca.* 650 ppm for one and *ca.* 400 ppm for the other. The former contains slightly less Fe but more Al and has a lower analytical sum than the latter, reflecting a

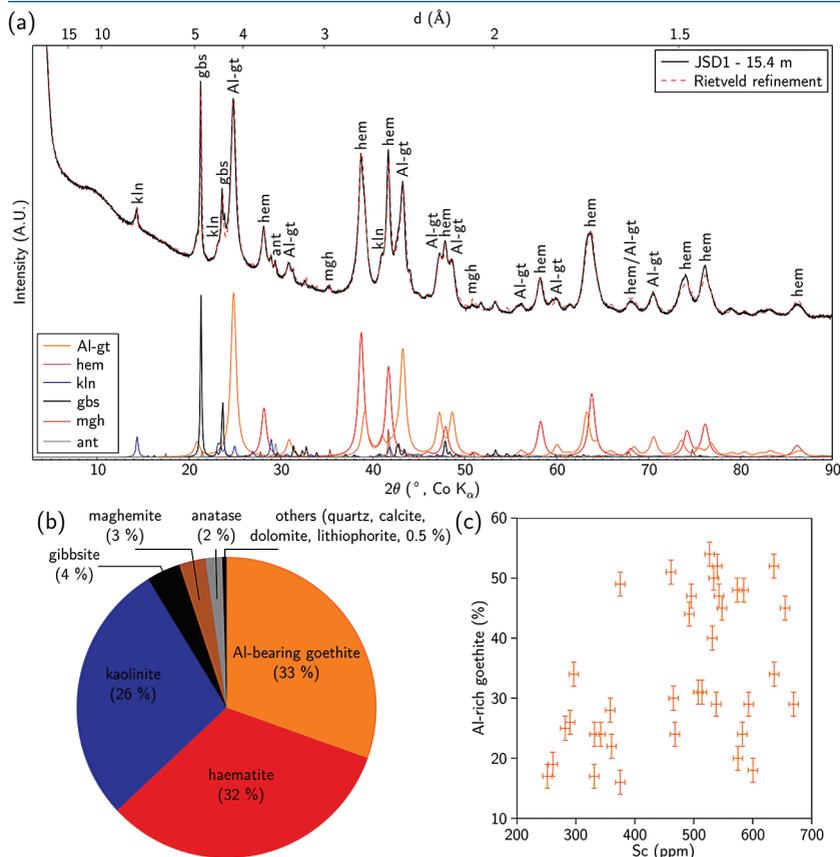


Figure 2 (a) X-ray diffraction pattern of ore sample JSD-1 – 15.4 m and associated multiphase Rietveld refinement (Al-gt: Al-bearing goethite, hem: haematite, kln: kaolinite, gbs: gibbsite, mgh: maghemite, ant: anatase). (b) Average phase proportions in the samples calculated from Rietveld refinement. (c) Bulk Sc concentration versus proportion of Al-bearing goethite estimated from Rietveld refinement.



higher goethite component. A third type of matrix is slightly enriched in both Al and Si, which is consistent with the presence of minor kaolinite mixed with Fe oxides. The Sc content of this matrix is *ca.* 400 ppm, which suggests that kaolinite is only a minor Sc host.

To distinguish between goethite and haematite, we also used Fe K-edge XANES spectra. Using the relative normalised intensity of the absorption maxima of goethite and haematite, at 7133.8 eV and 7136.9 eV, respectively (Combes *et al.*, 1989), we obtained Fe-speciation maps (Fig. 3a). Comparison with μ -XRF maps of Sc (Fig. 3b) indicate that Sc-poor and Sc-rich grains mostly contain haematite and goethite, respectively. Iron K-edge XANES spectra in the complete range of energy confirm these observation (Fig. 4a), showing a good match between spectra of goethite and Sc-rich zones and between spectra of haematite and Sc-poor zones.

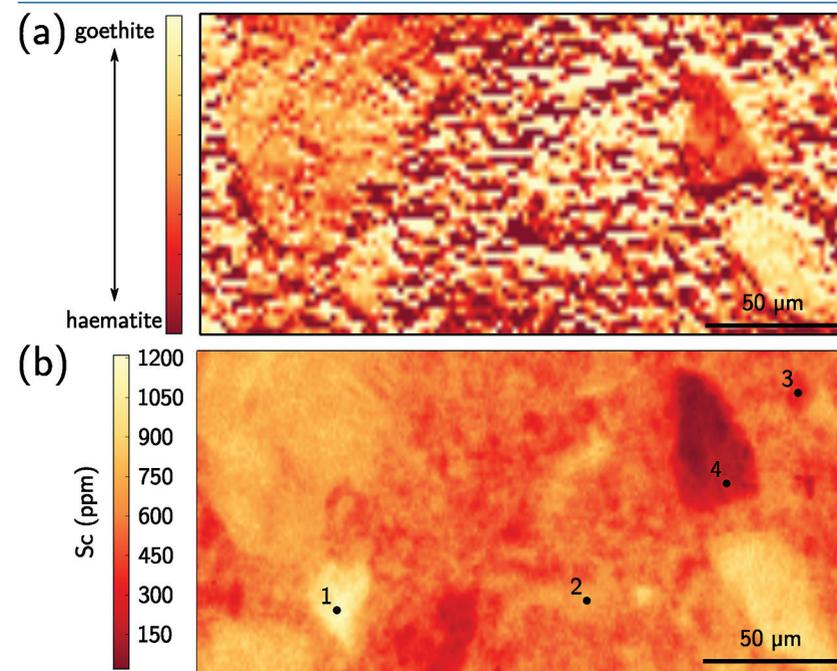


Figure 3 (a) Map of Fe speciation obtained by subtracting normalised synchrotron μ -XRF maps at 7133.9 eV, the energy characteristic of goethite and 7136.7 eV, the energy characteristic of haematite. (b) Synchrotron μ -XRF mapping of Sc.



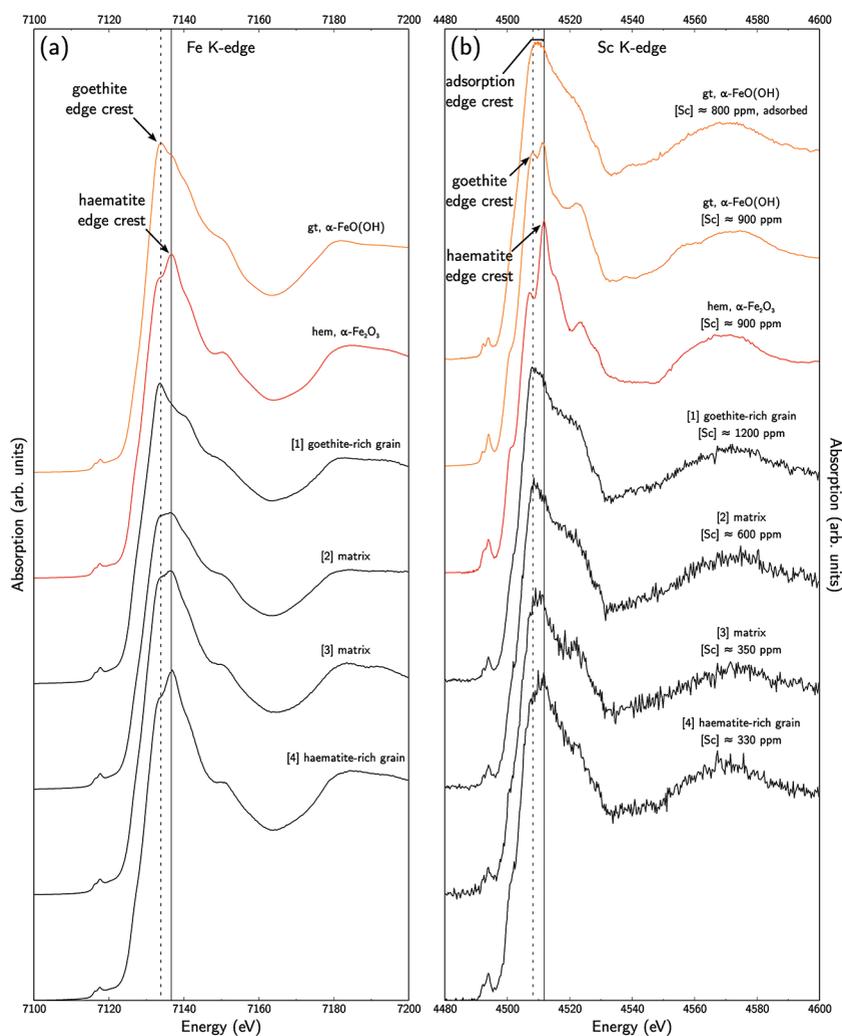


Figure 4 XANES spectra at the (a) Fe K-edge. (b) Sc K-edge (gt: goethite and hem: haematite). The numbers in brackets refer to the position given in Figure 3.

Using the EMP-derived Sc concentration in goethite, around 1300 ppm, and the proportion of goethite obtained from Rietveld refinement, about 30 %, we calculate that goethite hosts about 400 ppm Sc out of the average *ca.* 500 ppm of Sc in the samples, *i.e.* *ca.* 80 % of total Sc. Average EMP-derived concentrations

in haematite are about 200 ppm Sc. As haematite accounts for about 30 % of the mineral phases, Sc in haematite may represent *ca.* 50 ppm, corresponding to most of the remaining 20 % of total Sc.

Scandium Speciation in the Ore

Scandium K-edge XANES spectra of synthetic reference materials show that Sc incorporation in goethite or in haematite can be distinguished using the position of the edge crest at 4508.2 eV and 4511.8 eV, respectively (Fig. 4b), while Sc adsorbed on goethite is identified by a broad, featureless edge crest extending from 4508 eV to 4511.5 eV. On the low energy side, a pre-edge feature bears additional information (*e.g.*, Galois *et al.*, 2001). There is a noteworthy enhancement of the intensity of this feature in the substituted samples due to the distortion of the Sc site. The Sc K-edge XANES spectra on lateritic goethite grains show a broad edge crest and a low-intensity pre-edge feature, consistent with Sc adsorbed on goethite. In contrast, lateritic haematite grains show an edge crest at 4512 eV and a more intense pre-edge feature, corresponding to Sc incorporated in haematite. The same distinction holds when investigating the matrix: the high Sc concentrations are associated with Sc-adsorbed goethite. However, lateritic samples give less resolved spectra than the crystalline references. Comparison is limited because Sc K-edge XANES spectra are scarce in the literature, but this may reflect a poor crystallinity in fine-grained natural phases, or some minor contribution of other Sc species.

A Mechanism for Scandium Enrichment

Due to the high concentration of Sc in clinopyroxenes, weathering leads to Sc-rich waters circulating in the regolith below the water table. Seasonal precipitation of goethite allows the adsorption of Sc^{3+} . During dry periods, haematite develops from goethite, and may incorporate part of the adsorbed Sc in its crystal structure. However, this process is limited by the size difference between six-fold coordinated Sc^{3+} and Fe^{3+} but such size differences will not influence the adsorption capacity of goethite under near-neutral pH conditions.

Scandium is often associated with the rare earth elements (REE). The ionic radius of Sc^{3+} is slightly smaller than those of heavy REE for the same coordination number. During lateritic weathering of ultramafic–mafic rocks, Sc behaves like the heavy REE. The enrichment factor of Sc between the ore and fresh saprolite is *ca.* 5 (Table S-5, Fig. S-2). For the REE, it increases continuously with decreasing ionic radii, from *ca.* 2 for the light REE to *ca.* 3.5 for the heavy REE. The low prospectivity of the lateritic deposits for REE reflects the low REE content in the parent rock compared to average crustal concentrations (two to ten times lower, Rudnick and Gao, 2014).



Lateritic profiles over ultramafic–mafic rocks usually show Sc concentrations lower than 100 ppm, corresponding to enrichment by a factor of ten during lateritic weathering (Aiglsperger *et al.*, 2016; Maulana *et al.*, 2016). This is similar to the maximum factor of enrichment found in the Syerston–Flemington deposit where the limonitic laterite reaches 800 ppm Sc compared to *ca.* 80 ppm in the parent rock. This observation rules out any need for peculiar lateritic conditions in Eastern Australia, and the proposed genetic model for Sc concentration during lateritic weathering may thus be extrapolated to other lateritic deposits developed over ultramafic–mafic rocks. Nonetheless, the duration of the weathering process and tectonic stability are key factors leading to the development of such volumes of ore.

Exceptional concentration of Sc in lateritic deposits thus results from a combination of three circumstances: (1) anomalously high Sc concentration in the parent rock, (2) long time scales of alteration in stable tectonic environment and (3) lateritic conditions during weathering, allowing the trapping of Sc by Fe oxides.

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Additional Information

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