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Iron oxide minerals in dust of the Red Dawn event in eastern Australia, September 2009

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ABSTRACT

Iron oxide minerals typically compose only a few weight percent of bulk atmospheric dust but are important for potential roles in forcing climate, affecting cloud properties, influencing rates of snow and ice melt, and fertilizing marine phytoplankton. Dust samples collected from locations across eastern Australia (Lake Cowal, Orange, Hornsby, and Sydney) following the spectacular "Red Dawn" dust storm on 23 September 2009 enabled study of the dust iron oxide assemblage using a combination of magnetic measurements, Mössbauer spectroscopy, reflectance spectroscopy, and scanning electron microscopy. Red Dawn was the worst dust storm to have hit the city of Sydney in more than 60 years, and it also deposited dust into the Tasman Sea and onto snow cover in New Zealand. Magnetization measurements from 20 to 400 K reveal that hematite, goethite, and trace amounts of magnetite are present in all samples. Magnetite concentrations (as much as 0.29 wt%) were much higher in eastern, urban sites than in western, agricultural sites in central New South Wales (0.01 wt%), strongly suggesting addition of magnetite from local urban sources. Variable temperature Mössbauer spectroscopy (300 and 4.2 K) indicates that goethite and hematite compose approximately 25–45% of the Fe-bearing phases in samples from the inland sites of Orange and Lake Cowal. Hematite was observed at both temperatures but goethite only at 4.2 K, thereby revealing the presence of nanogoethite (less than about 20 nm). Similarly, hematite particulate matter is very small (some of it $d < 100$ nm) on the basis of magnetic results and Mössbauer spectra. The degree to which ferric oxide in these samples might absorb solar radiation is estimated by comparing reflectance values with a magnetic parameter (hard isothermal remanent magnetization, HIRM) for ferric oxide abundance. Average visible reflectance and HIRM are correlated as a group ($r^2 = 0.24$), indicating that Red Dawn ferric oxides have capacity to absorb solar radiation. Much of this ferric oxide occurs as nanohematite and nanogoethite particles on surfaces of other particulate matter, thereby providing high surface area to enhance absorption of solar radiation. Leaching of the sample from Orange in simulated human-lung fluid revealed low bioaccessibility for most metals.

1. Introduction

During the early hours of September 23rd, 2009, a large dust storm emanating from the lower Lake Eyre Basin of South Australia, western New South Wales (NSW) and southwestern Queensland engulfed eastern Australia along a 3000 km front (Supplementary data Fig. 1). As described by Leys et al. (2011), this was the worst dust storm to have hit the east coast city of Sydney in more than 60 years, with visibility reduced to less than 1 km for approximately 4 h and exceedingly large concentrations of suspended particulates recorded. The Sydney media quickly dubbed this event "Red Dawn" in recognition of the distinctly reddish hue of the dust pall that shrouded the city in the first few hours after sunrise on September 23rd (Leys et al., 2011).

The cause of this reddish hue of the plume was undoubtedly the presence of iron oxide and oxyhydroxide minerals in the dust (Radhi et al., 2010a). Such minerals are important components of lithogenic sediment in dusts, and typically include the Fe^{3+}

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minerals, hematite (αFe_2O_3) and goethite ($\alpha FeOOH$) (Shi et al., 2012). These two minerals (hereafter collectively referred to as iron oxides or ferric oxides) may occur separately or together in dust plumes in amounts as much as several percent by weight (Walker and Costin, 1971; Formenti et al., 2011; Maher, 2011). In Australia, vast tracts of the arid interior are characterised by the presence of wind-erodible sediments containing iron oxide compounds (CSIRO, 1983; Bullard and White, 2002). Morphologically, much of this iron oxide material is present in mineral dust as a component of thin clay coatings around quartz grains (Bullard and White, 2005). The field identification of these iron-rich clay coatings was used, in the past, by Australian soil surveyors to distinguish aeolian-derived sediments from those of fluvial origin; the name used locally to describe quartz grains covered in a veneer of iron-rich clay was "wustenquartz" (e.g., Sleeman, 1964). The commonly tattered coatings present in wustenquartz were assumed to reflect abrasion during transport and to indicate that these were not formed pedogenically after deposition (Sleeman, 1964). Iron oxides may also be present in dust as discrete nano-scale particles (Maher, 2011), but due to their size they have been rarely measured or reported as such.

Beyond providing a visual spectacle during dust storms and conferring reddish hues to dust-affected soil profiles, iron oxides in dusts are now identified as being important for a number of other environmental and biological processes. In particular, dust particles have properties of composition, size, and shape that can reflect, scatter, or absorb solar radiation, thereby cooling or heating the atmosphere and influencing atmospheric circulation (Pérez et al., 2006; Balkanski et al., 2007; IPCC, 2007). Certain iron oxide minerals, especially ferric oxides, have strong capacity to absorb solar radiation (Tegen et al., 1997; Sokolik and Toon, 1999; Lafon et al., 2006; Qin and Mitchell, 2009; Redmond et al., 2010). Layers of dust on snow and ice cover accelerate the melting of snow and ice by diminishing surface albedo (Painter et al., 2010), and the heat-absorbing properties of ferric oxide minerals in these dust layers can add to this effect (Reynolds et al., 2013). Moreover, iron-bearing dust provides nutrients for the fertilisation of marine phytoplankton, with consequential and possibly important drawdown of atmospheric CO_2 (Jickells et al., 2005; Gassó et al., 2010; Shao et al., 2011; Nickovic et al., 2013). Different dust compositions can variably affect biogeochemical cycles and the delivery of nutrients to terrestrial ecosystems (e.g., Koren et al., 2006), although the roles of iron in these influences remains little studied. Importantly, iron oxide minerals from source sediments can be altered through atmospheric processes and mixing of aerosols from natural and industrial sources during atmospheric transport, thereby producing new aerosols that can further influence climate, cloud formation, and ocean fertilization involving especially the solubility of iron-bearing particles (Gassó et al., 2010).

Finally, dust during this and preceding widespread events likely have important bearing on human health especially with regard to the effects of small particulate matter (PM) on respiratory function (Chan et al., 2005). Concern exists about other effects of dust on human health related to particle composition and shape (Plumlee and Ziegler, 2007; Giannadaki et al., 2013). Such concern is an emerging area of medical research that investigates the effects of metals, including iron, in dust on human epithelial respiratory cells and on lung disease (e.g., Ghio et al., 1992; Turi et al., 2004; Schoonen et al., 2006; Reid et al., 2009). Medical science has only recently started to investigate components in desert-derived dust for effects on inflammation in lungs.

The forms and attributes of iron oxide minerals have received relatively little detailed study. Particle size, reflectance, solubility, and bioaccessibility of iron oxides in dust will determine the ultimate influences of these materials on environmental and biological processes. Samples of dust deposited across eastern Australia during the Red Dawn dust-storm events in September 2009 provide an ideal opportunity to examine some physical and mineralogic properties of such iron oxides. Using a suite of reflectance spectroscopy, Mössbauer spectroscopy, magnetic property, and electron microscopy methods, the primary aim of this study was to identify iron oxide minerals and their particle sizes in some samples of Red Dawn dust. A secondary aim was to investigate the solubility of dust-borne metals, including iron from well-characterized iron oxide minerals, in a fluid that simulates human lung fluid.

2. Materials and methods

2.1. Dust samples

A small number of dust samples were collected opportunistically from various locations in NSW following the Red Dawn event of September 2009. As indicated in Table 1 and Supplementary data Fig. 2, the six Lake Cowal (LC) samples were obtained from locations approximately 350 km W of Sydney, the Orange sample was obtained approximately 200 km WNW of Sydney, and the other three samples (Hornsby, Fisher, and St. Peters) were obtained from locations in greater Sydney. The relatively high mass (2.1 g) of the Orange sample allowed a wide range of analytical procedures. Lesser mass of the other samples limited their analyses. The six LC samples were monthly deposits collected from inverted frisbee dust gauges (Sow et al., 2006) already established as part of a long-term dust monitoring study. Although it is inevitable that these dust samples will have contained some material not transported during the Red Dawn event, the amounts of dust captured in the gauges during the sampling period of Red Dawn were between two and three times more than average monthly values for these gauges (Cattle et al., 2012), suggesting that Red Dawn dust was the dominant component of these samples. Of these six gauges, four (LC1–LC4) were located at increasing distances downwind of an open-cut gold mine (Cowal Gold Mine), and two were located essentially upwind (dominant direction) of the mine (LC5–LC6). With the exception of LC1, the main particle sizes of the LC samples, as identified by high-resolution particle-size analysis with a Coulter Multisizer 3, were a very fine silt-sized population (5–20 μm), a clay-sized fraction (<3 μm), and in some cases a coarser silt-sized population (30–50 μm) (Table 1; Supplementary data Fig. 3). The LC1 sample was dominated by a coarse silt-sized population and an assortment of fine sand-sized particles (50–100 μm). The Orange sample was collected from a large, flat pool deck the day after the Red Dawn event. The main particle population of this sample was very fine silt-sized (5–15 μm) and very similar to those of the LC samples. Due to the opportunistic nature of sampling in Sydney (e.g., from car windscreen, balcony), the amounts of dust collected were generally very small. The Hornsby sample, taken from a car windscreen in a peri-urban location, contained a broad population of silt-sized particles (5–50 μm) and a distinct population of fine sand-sized particles (100–200 μm), presumably of local origin. The Fisher sample, taken from a clean plastic tray installed on a multi-storey building roof on the morning of the Red Dawn event, comprised a coarse silt-sized particle population (20–60 μm) and a conspicuous range of fine sand-sized particles (60–200 μm), also presumably of local origin. The St. Peters sample was obtained from a balcony of an apartment building the day after the Red Dawn event, and contained a prominent silt-sized particle population (15–30 μm) along with a minor, very fine silt-sized population (5–15 μm).

2.2. Scanning electron microscopy

We examined dust particles from the Orange sample at resolutions above 9 nm using Scanning Electron Microscopy (SEM; FEI