



Research paper

Caesium incorporation and retention in illite interlayers



Adam J. Fuller ^{a,1}, Samuel Shaw ^b, Michael B. Ward ^c, Sarah J. Haigh ^{d,e}, J. Frederick W. Mosselmans ^f,
Caroline L. Peacock ^a, Stephen Stackhouse ^a, Andrew J. Dent ^f, Divyesh Trivedi ^g, Ian T. Burke ^{a,*}

^a School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

^b School of Earth, Atmospheric and Environmental Science, University of Manchester, Manchester M13 9PL, UK

^c Leeds Electron Microscopy and Spectroscopy Centre, School of Process Environmental and Materials Engineering, University of Leeds, LS2 9JT, UK

^d SuperSTEM, STFC Daresbury Laboratories, Keckwick Lane, Warrington WA4 4AD, UK

^e School of Materials, University of Manchester, Manchester M13 9PL, UK

^f Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK

^g National Nuclear Laboratory Ltd., Chadwick House, Warrington Road, Birchwood Park, Warrington WA3 6AE, UK

ARTICLE INFO

Article history:

Received 11 November 2014

Received in revised form 6 February 2015

Accepted 8 February 2015

Available online 23 February 2015

Keywords:

Cs

TEM

Illite

DFT

EXAFS

ABSTRACT

Radioactive caesium (chiefly ¹³⁷Cs) is a major environmental pollutant. The mobility of Cs in temperate soils is primarily controlled by sorption onto clay minerals, particularly the frayed edges of illite interlayers. This paper investigates the adsorption of Cs to illite at the molecular scale, over both the short and long term. Transmission electron microscopy (TEM) images showed that after initial absorption into the frayed edges, Cs migrated into the illite interlayer becoming incorporated within the mineral structure. Caesium initially exchanged with hydrated Ca at the frayed edges, causing them to collapse. This process was irreversible as Cs held in the collapsed interlayers was not exchangeable with Ca. Over the long term Cs did not remain at the edge of the illite crystals, but diffused into the interlayers by exchange with K. Results from extended X-ray absorption fine structure spectroscopy (EXAFS) and density functional theory modelling confirmed that Cs was incorporated into the illite interlayer and revealed its bonding environment.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The ubiquity of ¹³⁷Cs in nuclear waste means that it is one of the most common radionuclides released into the environment by human action. Once released, the relatively long half-life ($t_{1/2}$ 30 years) and large dose rate of ¹³⁷Cs mean that it poses a potential long term radiation risk. The nuclear accidents at Chernobyl, and more recently at Fukushima, demonstrated this most acutely. In both these cases, radiocaesium remains the key contributor to radioactive dose and the reason for maintaining the exclusion zone (Jacob et al., 2009; Kinoshita et al., 2011). Additionally ¹³⁷Cs is a common contaminant at nuclear sites, such as Hanford and Sellafield, due to historic releases (Chorover et al., 2008; Reeve and Eilbeck, 2009).

Caesium is highly soluble and is present in groundwater as the monovalent Cs⁺ cation under all conditions of Eh and pH. Due to this, its concentration in solution (and thus its environmental mobility) is primarily controlled by retention on the surfaces of soil minerals, primarily through cation exchange (Sawhney, 1972; Cornell, 1993;

Hird et al., 1996). Caesium does not readily adsorb onto iron oxide minerals (Todorovic et al., 1992; Wang et al., 2000) and it is therefore principally adsorbed on clay mineral surfaces (especially in organic poor soils) (Grutter et al., 1990; Shenber and Eriksson, 1993b; Chibowski and Zygumnt, 2002). However, the sorption behaviour of Cs varies greatly between the different clay minerals and the different exchange sites on those clays. Caesium adsorption to clays occurs via several different mechanisms, including outer-sphere adsorption to planar surfaces, edge adsorption and intercalation into structural sites (Jacobs and Tamura, 1960; Hird et al., 1996; Bradbury and Baeyens, 2000). Here, and throughout this paper, outer-sphere adsorption is defined as electrostatic bonding of a hydrated ion to a surface, inner-sphere adsorption as direct bonding (electrostatic or covalent) of the dehydrated ion to the surface reactive site and absorption as incorporation into the clay structure (including within a collapsed interlayer). The dominant adsorption process within a particular environment, is dependent on a number of factors, including Cs concentration, clay structure and solution pH (Fuller et al., 2014). Multiple studies have shown that Cs is preferentially removed from solution and retained on the surfaces of soil minerals even when the total ionic-strength of other cations is very high (Brouwer et al., 1983; Dyer et al., 2000; Chorover et al., 2008). Studies from soils with varying mineralogy showed that this selective adsorption and retention of Cs was occurring primarily on illite

* Corresponding author. Tel.: +44 113 3437532.

E-mail address: i.t.burke@leeds.ac.uk (I.T. Burke).

¹ Present address: Centre for Radiochemistry Research, School of Chemistry, University of Manchester, Manchester, M13 9PL.

(K,Ca,Mg) (Al,Mg,Fe)₂ (Si,Al)₄ O₁₀ [(OH)₂,(H₂O)] (Cremers et al., 1988). The illite structure consists of 2:1 layers with two Si/Al tetrahedral sheets and a central octahedral sheet (Si/Al/Fe/Mg) which are bound together by interlayer cations. Illite commonly has K in its interlayer site which yields an overall basal spacing of 1.0 nm. However, other monovalent and divalent cations are able to exchange with the K ions and distort the structure. Most commonly illite weathers to vermiculite via the exchange of K ions for Ca (Jackson et al., 1952). As Ca is strongly hydrated it retains its waters of hydration in the interlayer causing an expansion of the illite basal spacing to 1.4 nm (Jackson et al., 1952; Jackson, 1968). This Ca weathering yields a partially expanded wedge zone between the hydrated and dehydrated interlayers, commonly called the frayed edge (Nakao et al., 2008). These frayed edge sites have been shown to selectively adsorb Cs, in preference to other monovalent and divalent cations (Chorover et al., 2008; Nakao et al., 2008). It has also been shown that once caesium is adsorbed into the frayed edge sites it cannot be readily desorbed back to solution, making these sites extremely important in controlling the long term retention of Cs in the environment, and controlling its mobility (Comans et al., 1991; de Koning and Comans, 2004). Frayed edges may also occur on other micaceous clays (McKinley et al., 2004; Wampler et al., 2012), however Cs is not as strongly held on these non-illitic frayed edges as it is in illite (Ohnuki and Kozai, 2013). Poinssot et al. (1999) and Sawhney (1966) showed that this sorption to the illite frayed edge sites was controlled by kinetics, taking more than a year to reach sorption equilibrium. To explain this Comans et al. (1991) and Comans and Hockley (1992) speculated that uptake occurs via a two stage adsorption process with both rapid cation exchange onto frayed edge sites and a much slower mechanism, potentially involving the illite interlayer spaces. Caesium is known to be able to absorb into the interlayer of expanding clays but via different mechanisms. Specifically Cs is weakly adsorbed electrostatically in outer-sphere complexes (through interstitial waters) in the hydrated interlayer of montmorillonite (Bostick et al., 2002; Ohnuki and Kozai, 2013). It can also absorb into the interlayer space of vermiculite, in inner-sphere complexes, potentially due to a collapse of the interlayer space, or the presence of a frayed edge (Bostick et al., 2002; Wampler et al., 2012). In addition to these interlayer sorption processes Cs is also known to adsorb via simple cation exchange onto the permanent charge sites on the clay basal plane. This process is not ion specific and is strongly controlled by solution ionic strength (Fuller et al., 2014).

Although previous authors have offered a detailed description of macro-scale Cs adsorption on illite; there is a significant gap in understanding the molecular-scale mechanisms governing these observations. However, significant advances have been made in recent years on understanding the sorption of Cs to other closely related micaceous minerals at the molecular scale. Most of this work has relied on High Resolution Transmission Electron Microscopy (HRTEM). McKinley et al. (2004) were the first to show the potential of TEM imaging to identify the site of Cs adsorption in biotite and muscovite. They showed that Cs accumulated around the edge of microscopic (many hundreds of microns across) biotite crystals. They were also able to observe inclusions of Cs deeper in the crystal, but attributed this to the presence of frayed edges at intra-particle defects. They were not able to observe any migration of Cs into the interlayer space, due to the short time period of the experiments (Comans and Hockley, 1992). More recently, work by Kogure et al. (2012), Okumura et al. (2014), and Tamura et al. (2014) has successfully shown that Cs is able to penetrate deep into the hydrated interlayer of both vermiculite and phlogopite. Specifically, Kogure et al. (2012) directly observed that Cs was incorporated into the vermiculite interlayer via exchange with hydrated Mg ions. Tamura et al. (2014) observed this same process occurring on a Mg altered phlogopite. Interestingly they noted that Cs would not readily exchange for the dehydrated K in interlayer spaces of natural (unaltered) phlogopite. They suggested that this process may be kinetically hindered (as previously suggested by Comans and Hockley (1992)) and that the equilibrium times within their experiments were not

long enough. Okumura et al. (2014) recently presented direct observation of Cs exchange for K-phlogopite interlayer spaces. They observed that Cs did not uniformly exchange all interlayers but favoured some over others. They suggested that this may be due to inhomogeneity within the clay structure, and stressed the importance of determining if this process occurred in other micaceous clays (with a different 2:1 layer structure). Therefore, although significant advances have been made in recent years in understanding Cs incorporation into mica; it remains an unanswered question whether these same processes are controlling the long term sorption and retention of Cs in illite. This is particularly important as Cs is adsorbed and retained by illite in preference to other ions (Poinssot et al., 1999; Steefel et al., 2003) and so long term Cs behaviour at many contaminated sites (such as Sellafield in the UK) is known to be controlled primarily by illite (Randall et al., 2004; Dutton et al., 2009).

This paper has two key aims. Firstly, to directly characterise the nature of the illite frayed edge and determine the mechanism of Cs adsorption therein. Secondly, to understand the migration of Cs deeper into the illite interlayer space. This work is driven by the hypothesis that the same interlayer incorporation mechanism observed in other micaceous clays occurs in illite. However, it has been shown that Cs takes a long time to reach equilibrium with the illite interlayer, likely due to stronger interlayer forces in illite than in previously studied clays. Therefore to ensure that sufficient concentrations of Cs were taken into the illite structure the experiments in this study were performed for long time periods (up to 1 year) and with a high Cs concentration (to increase the kinetic driving force, consistent with other authors (Kogure et al., 2012; Okumura et al., 2014; Tamura et al., 2014)). Previous microscopy studies have focused simply on the end point of Cs incorporation. However, this paper addresses the entire sorption process, from initial sorption on the frayed edge to its long term fate therein. This atomic-scale mechanistic understanding was achieved by utilising aberration corrected (scanning) transmission electron microscopy ((S)TEM), energy dispersive X-ray spectroscopy (EDX) and extended X-ray absorption fine structure spectroscopy (EXAFS), coupled with density functional theory (DFT) modelling.

2. Materials and methods

2.1. Materials

All the experiments described in this paper were conducted using Illite IMT-1, (Mg_{0.09} Ca_{0.06} K_{1.37}) [Al_{2.69} Fe(III)_{0.76} Fe(II)_{0.06} Mn_{tr} Mg_{0.43} Ti_{0.06}] [Si_{6.77} Al_{1.23}]O₂₀(OH)₄ (Hower and Mowatt, 1966) purchased from the Clay Minerals Society Source Clay Repository. This is a well characterised reference mineral from the Silver Hills, Montana, USA. To maximise the available surface area and create fresh unfrayed edges, the sample was finely crushed to <63 μm with a pestle and mortar and the particle size was verified by sieving. A 0.1 g subsample of the crushed illite was then weathered by suspension in a 0.1 mol L⁻¹ CaCl solution for one week, shaken daily. The remaining material was utilised without any chemical treatment.

Experiments were conducted with analytical grade reagents (or above) obtained from Fischer Scientific. Specifically, the CsCl was obtained as a dehydrated powder with 99.999% purity. The CaCl was obtained as CaCl₂·2H₂O powder with purity of >99.0%. The chemicals were used as received.

2.2. Batch sorption

Two distinct experimental systems were established, a system to test the short term adsorption/desorption of Cs on the Ca-weathered illite and a long term system to investigate the incorporation of Cs into the un-weathered K-interlayer.

To investigate the sorption of Cs onto the frayed edge sites the 0.1 g sample of the Ca-weathered illite was suspended in 1.0 mol L⁻¹ CsCl at

Download English Version:

<https://daneshyari.com/en/article/8046532>

Download Persian Version:

<https://daneshyari.com/article/8046532>

[Daneshyari.com](https://daneshyari.com)