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Mineralogical sources of groundwater fluoride in Archaen bedrock/regolith aquifers: Mass balances from southern India and north-central Sri Lanka

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ABSTRACT

Study region: The Maheshwaram and Waipally catchments of Andhra Pradesh, India, and the Plonnaruwa catchment of north-central Sri Lanka.

Study focus: The distribution of F across eight crystalline phases and between the bedrock and the regolith at eleven sites in three catchments is documented. Mineral contributions to F release during weathering and regolith development are quantified.

New hydrological insights for the region: An estimate of weathering duration for the in situ regolith in Andhra Pradesh, 250–380 Ka, is close to a previous estimate for southern India. Partial or total destruction of the primary F-bearing bedrock minerals and consistent depletion of F in the remnant minerals result in a much reduced total F content in the regolith. Leaching experiments and field relationships, however, indicate a greater potential for F mobilisation to groundwater from the regolith than the bedrock. Schemes for managed aquifer recharge should beware the risk of mobilising additional F to groundwater.

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1. Introduction

Regionally extensive occurrences of excessive groundwater fluoride (F^-) are found on all the populated continents (Amini et al., 2008) and more than 200 million people worldwide use groundwater-sourced drinking water with F^- concentrations above the WHO guideline value of 1.5 mg/l (UNICEF, 2008). Excessive F^- causes fluorosis in humans (Fawell et al., 2006) and with drinking water the primary route for fluoride ingestion, an association between the levels of groundwater F^- and the incidence and severity of fluorosis has been identified widely across regions where untreated groundwater provides the principal water supply (Amini et al., 2008), notwithstanding that diet may be a mitigating factor (Susheela and Bhatnagar, 2002). In both India (Chakraborti et al., 2011) and Sri Lanka (Dissanayake, 1991) fluorosis is the most widespread disease of geogenic origin, and its link to excessive F^- in groundwater is well established (Nayak et al., 2009). In India alone, more than 65 million people suffer from fluorosis related to F^- in drinking water (Ayoob and Gupta, 2006).

Despite the potential influence of F^- enrichment in irrigation return flow (Pettenati et al., 2013), groundwater host-rocks are acknowledged as the principal sources of regionally extensive F^- (Edmunds and Smedley, 2005) with mobilisation of F^- to groundwater in the crystalline bedrock/regolith terrain of India and Sri Lanka (Mukherjee et al., 2015) ultimately being the consequence of bedrock weathering and regolith development. 'Bedrock' here refers to the unaltered Pre-Cambrian basement rock in which tectonic fractures and/or fracturing related to lithostatic decompression may be present, providing the bedrock with its limited permeability and very low porosity. 'Regolith' is taken to include the weathered material overlying the fresh bedrock, the product of prolonged in situ chemical alteration of bedrock in which porosity and storativity are much enhanced relative to that of the parent bedrock. A zone of fracturing may also be present at the base of the regolith, which provides a moderate permeability where present and is proposed by Lachassagne et al. (2011) in their critical analysis of fracturing in hard rock aquifers to be the consequence of early stage weathering-induced volumetric increase. Chemical weathering by hydrolysis and redox reaction drives the alteration of primary bedrock minerals and the release of inorganic ions to aqueous solution; neoformation of authigenic minerals and sorption of released ions will proceed according to solubility controls and surface reaction processes (Drever, 1997). Dewandel et al. (2006) provide a quantitative description of the hydraulic characteristics of the weathering profile to bedrock for the Maheshwaram catchment of Andhra Pradesh, India, including the fractured layer at the base of the regolith, and infer a polyphase sequence of weathering and erosion to explain the occurrence of relic fractures within the weathered regolith. These interpretations of the role of weathering in regolith development in Andhra Pradesh provide a basis for the designation of samples in the present study, considered further in Section 3 below.

The many common minerals which contain F, and the wide variety of F-bearing lithologies are well known (Jeffery and Hutchinson, 1986; Edmunds and Smedley, 2005). Yet in Pre-Cambrian crystalline bedrock/regolith terrain, which constitutes a strategically important aquifer environment in India and Sri Lanka, uncertainties persist in relation to the relative contribution of the different F-bearing minerals, their distribution between the bedrock and the regolith, and even the relative significance of the bedrock and regolith as sources of fluoride to groundwater.

Many accounts exist of the spatial variability of groundwater F^- in affected catchments (Amini et al., 2008). Reddy et al. (2010) propose that spatial variations in bedrock–regolith mineralogy and F content are responsible for observed differences in groundwater F^- concentration between and within discrete catchments. Elsewhere, consistent increases in groundwater F^- down-gradient along valley profiles have been related to geochemical control (Jacks and Sharma, 1995; Reddy et al., 2010), precipitation of calcite and dolomite allowing groundwater F^- concentration to rise under fluorite solubility control. In Sri Lanka, where geological and climatic boundaries are approximately orthogonal, a dominant climatic control has been proposed to explain the coincidence of high groundwater F^- with the dry zone, and vice versa (Dissanayake, 1991). Yet none of these studies report the mineralogical distribution of F, nor do they address the distinctions between bedrock and regolith F content and the possible implications for seasonal and/or secular trends in groundwater F^-.

A seasonal increase in groundwater F^- following the summer monsoon (e.g. Sreedevi et al., 2006), a secular increasing trend in groundwater F^- (e.g. Marechal et al., 2006), or both (Pettenati et al., 2013), have been widely speculated but sparsely recorded within the Pre-Cambrian crystalline bedrock/regolith aquifer environment. A variety of influences have been proposed in explanation, including seasonal fluctuation in groundwater levels (Sreedevi et al., 2006), human-induced modification of recharge, including anthropologically enhanced recharge as irrigation return flow (Pettenati et al., 2013), and long-term decline of groundwater levels due to intensive abstraction (Marechal et al., 2006, S.S.D. Foster, *pers. comm*). These explanations, implicitly or explicitly bearing on the lithological sources of the dissolved F^-, are in part inconsistent or contradictory. Sreedevi et al. (2006) imply the regolith and surficial soils to be the dominant sources of F^- which is mobilised by recharge. Foster (*pers. comm.*) links a posited widespread secular increase in groundwater F^- over the past 25 years (unrecorded in the scientific literature) to a general decline in groundwater level, a consequence of intensive abstraction for irrigation (Marechal et al., 2006). They imply that prolonged water–rock reaction in remnant pockets of groundwater stored within irregular depressions of the bedrock surface results in elevated groundwater F^-, with the bedrock as the principal source of F. Schemes to dilute groundwater F^- concentration through augmentation of groundwater recharge, a popular management strategy supported by international donor agencies, have been predicated on this concept that bedrock is the principal source of F^- (Rao, 2003; Bhagavan and Raghu, 2005). There is however an absence of evidence to discount the opposing view that the regolith is the main source for groundwater F^-; a possibility that risks artificial groundwater recharge schemes mobilising additional F^- and degrading groundwater quality.

Full consideration of this variety of contrasting hypotheses requires a quantitative knowledge of the mineralogical distribution of F within and between the bedrock and the derived regolith of the composite bedrock/regolith aquifer. In this paper we document the distribution of F in the crystalline mineralogical components of the Archaen gneissic bedrock and its associated regolith in three study areas (Fig. 1): two in Andhra Pradesh, southern India (Maheshwaram, Waipally), and one in north-central Sri Lanka (Plonnaruwa). In rural Andhra Pradesh, the state in India most severely affected by groundwater F^- (Mukherjee et al., 2015; Kulkarni et al., 2015), groundwater drawn from wells in the gneissic bedrock and weathered regolith of the Archaen Peninsular Granite commonly contains F^- at up to 4 mg/l e.g. at Maheshwaram (Sreedevi et al., 2006), in places up to 7 mg/l e.g. at Waipally (Reddy et al., 2010) and exceptionally as high as 20 mg/l (Rao et al., 1993). Groundwater F^- ranges from 1.5 to >5 mg/l in the Pre-Cambrian gneissic terrain of the Highland and Vijayan complexes of the north-central province of Sri Lanka (Dissanayake, 1991).

The primary objective is to quantify the potential mineralogical sources of groundwater F^- at the study sites in the present day, and the relative availability of F to groundwater from the bedrock and regolith as discrete components of the bedrock/regolith aquifer. We use the results to investigate relationships between F distribution in bedrock/regolith material and present-day groundwater F^-, spatially and seasonally with reference to existing data from the sites. A secondary objective is to indicate directly the mineralogical contributions to the flux of F during past regolith development. Thirdly, based on an inference of the cumulative groundwater flux, and other simplifying assumptions, the results allow a first estimate of the regolith weathering duration.

2. The study areas

The three study areas (Fig. 1), Maheshwaram and Waipally in Andhra Pradesh and Plonnaruwa in Sri Lanka, are located in catchments developed on outcropping Pre-Cambrian gneissic bedrock and associated regolith, selected on account of the availability of contextual data describing geology, aquifer structure, groundwater levels, and groundwater chemistry. In Andhra Pradesh the bedrock is formed of granitic gneisses of the Peninsular Granite Complex; in Plonnaruwa the bedrock is charnockitic gneiss of the Highland Complex. The Peninsular Granite Complex is represented by units mapped as Biotite Granite, Leucocratic Granite and Intermediate Granite in the Maheshwaram catchment (Geological Survey of India, 2002) and in the Wailpally catchment includes younger intrusives and massive granites as well as calcrete which is widely present throughout the regolith as fracture infill (Geological Survey of India, 1989). The Highland Complex at Plonnaruwa in Sri Lanka consists of charnockitic gneiss (Vitanage, 1959).

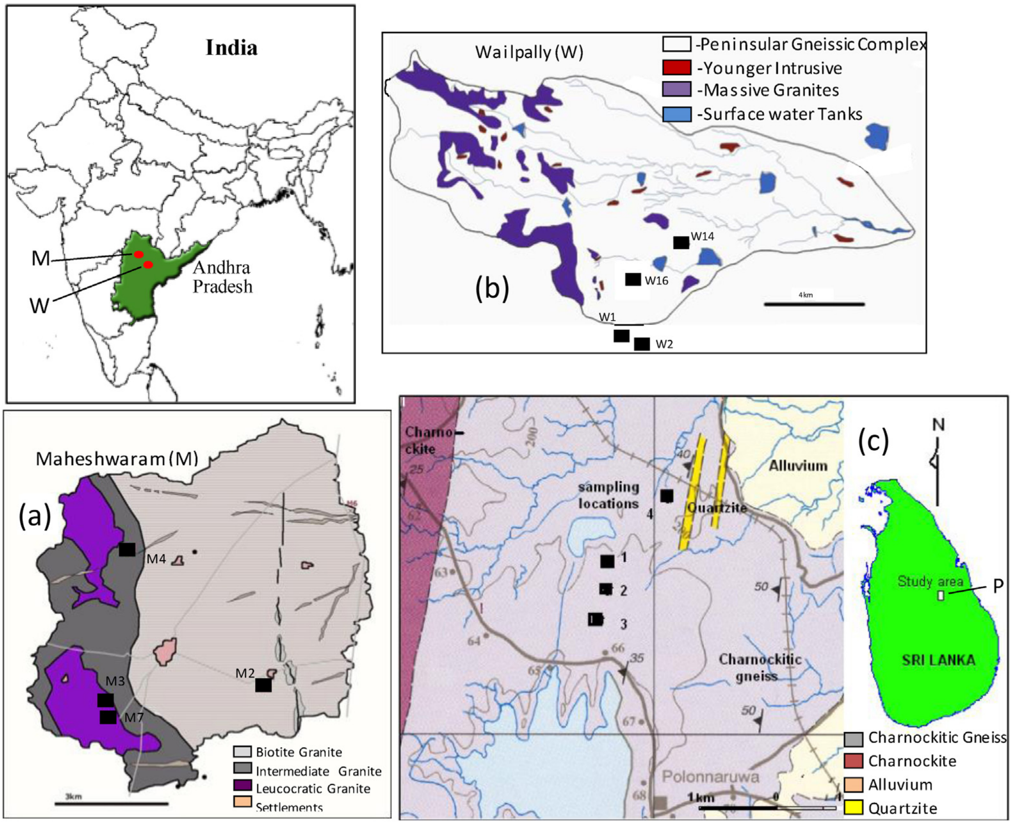

Fig. 1. Geology and sample locations at (a) Maheshwaram (M) and (b) Waipally (W), (Andhra Pradesh, India) and (c) Plonnaruwa (P) (Sri Lanka). Sample locations shown as black squares.

At Maheshwaram (as leucogranite) and Waipally (as massive granites), crystalline bedrock outcrops in elevated ground at the head of the catchments, reaching 670 m and 400 m amsl respectively. From the margins of the bedrock outcrops, and across the relatively flat catchment interiors falling to 590 m (Maheshwaram) and 280 m (Waipally), weathered regolith mantles an irregular surface of the fractured bedrock to about 10–20 m depth (Dhakate et al., 2008). At Plonnaruwa, bedrock forms small, discrete and irregular outcrops but is mostly covered by regolith to a maximum depth of about 10 m. Across all the catchments, groundwater flow generally follows the surface topographic gradient (Dhakate et al., 2008), altough the natural flow system is much perturbed by pumping for irrigation and domestic supply (Pettenati et al., 2013).

In Andhra Pradesh the climate is semi-arid to sub-tropical with an average annual rainfall of 812 mm in Maheshwaram and 632 mm in Wailpally, most of which falls in the monsoon season. Land use is predominantly agricultural, with high rates of groundwater abstraction used for irrigation. A quantitative description of the aquifer hydraulic structure at Maheshwaram by Dewandel et al. (2006) formed the basis for their proposal of a two-stage development of the regolith from bedrock. A generalised hydraulic model of the bedrock/regolith aquifer in Andhra Pradesh, recognising the regolith as an aquitard allowing vertical downward flow under conditions of intensive pumping from the bedrock, was described by Rushton (1986) at a time when the water table remained perennially within the regolith. Large scale groundwater-fed irrigation throughout Andhra Pradesh over the past 30 years has resulted in the water table declining into the fractured bedrock, leaving much of the regolith now largely dewatered (Kumar and Ahmed, 2003) and resulting in groundwater stagnation across parts of Maheshwaram (Marechal et al., 2006) and Waipally (Reddy et al., 2010). Groundwater [F^-] ranges in Maheshwaram from 0.40 to 4.27 mg/l (Sreedevi et al., 2006) and in Wailpally from 0.97 to 7.6 mg/l (Reddy et al., 2010). In both catchments the groundwater is under-saturated with respect to fluorite. In north-central Sri Lanka the water table is generally within the regolith, fluctuating seasonally between about 2 and 10 m below ground level; groundwater [F^-] at Plonnaruwa ranges from <1 to >5.0 mg/L.

3. Methodology

Eleven paired samples, each of 100–1000 g weight and representing as closely as possible the fresh bedrock and its associated regolith, were collected from outcrop and from accessible dry dug-wells in the Archaen Peninsular Granite Complex (4 paired samples each from Maheshwaram and Waipally) and the Highland Complex (3 paired samples from Plonnaruwa). Sample details are given in Table 1, and sample locations are indicated in Fig. 1. The samples incorporated the range of lithologies mapped as present in the Peninsular Granite Complex of the Maheshwaram and Waipally catchments, omitting the Younger Intrusives and Massive Granites at Waipally, and focussing on the extensive Charnockitic Gneiss at Plonnaruwa, Sri Lanka. The regolith samples were from that part of the weathering profile described as laminated saprolite by Dewandel et al. (2006). While the bedrock samples are taken to represent as closely as possible the fresh, unweathered, basement rock, even outcrop samples may in fact be from the fractured layer at the top of the true fresh basement, the fractures being generated during an early stage of weathering according to Dewandel et al. (2006). Some bedrock samples were collected from rock piles adjacent to dug wells, remnant from the time of excavation (Table 1), to which the same caveat of representivity applies. Specimens to represent bedrock were therefore collected from the inner, visually unweathered regions of the rock sample, and all exposed and/or weathered rims were chipped away at the time of sampling and discarded.

Samples were analysed by optical petrography, X-ray diffraction, and electron microscopy with electron backscatter detection (EM-EBSD) and energy dispersive X-ray detection (EM-EDX) to determine the crystalline phase mineral abundances and F contents. The fresh bedrock samples were classified (Table 1) according to the International Union of Geological Sciences (IUGS) rock classification scheme.

Optical petrography allowed mineral identification, measurement of mineral abundance by point-counting, visual characterisation of weathering and location of targets for electron microprobe analysis. Multiple determinations of mineral-specific F content were made on each sample by EM-EDX analysis. Whole-rock chemical analysis was performed using the Ingram (1970) method for F and ICP-AES for other elements. Leaching experiments were carried out to determine the relative availability of F from the bedrock and regolith as discrete components of the aquifer, following an approach adapted from Chae et al. (2006). At one site in each of the Andhra Pradesh catchments, additional samples for leaching experiments were collected at approximately 2-m depth intervals through the upper 7 m (Waipally) to 10 m (Maheshwaram) of the regolith, and so incorporating the sandy regolith in the upper 1–3 m of the weathering profile as well as the laminated saprolite as described by Dewandel et al. (2006). Samples were crushed and sieved to achieve the size fraction 0.5–2 mm, added to de-ionised water in a water–rock mass ratio of 1:5 in a plastic container and placed on a roller for continuous agitation at room temperature. Aliquots of leachate were extracted at regular intervals, and filtered prior to analysis. Full analytical details are given in Hallett (2012).

For each pair of samples, a mineralogical mass balance of F in the crystalline phases of the fresh rock and weathered regolith was determined by summing the contributions of each mineral. The gross quantity of F removed during the bedrock to regolith weathering process was calculated by difference. The mineralogical mass balances of F were used to compute the individual mineral contributions to F removal during the weathering of bedrock to regolith.

4. Results

Selected photomicrographs and EM-EBSD images (Fig. 2) illustrate the mineralogy of the bedrock and regolith of the study areas, and EM-EDX images (Fig. 3) illustrate the distribution of F within F-bearing crystalline phases. Mineral abundances, F contents and contributions to the whole rock F content are listed in Table 2 (Maheshwaram), 3 (Waipally) and 4 (Plonnaruwa) respectively. Mineral

Table 1
Sample location and contexts. CIA: chemical index of alteration (Nesbitt and Young, 1989). nd: not determined.

Sample	Location (decimal degrees)	Description	CIA	Mapped unit	
Andhra Pradesh, Maheshwaram					
M2a	Lat: 17.13 Long: 78.45	Porphyritic biotite granodiorite	50		Biotite Granite
M2b		Weathered equivalent of M2a, from dug well at 10 m depth	53.9		
M2x		Regolith profile samples, 1–10 m depth in dug well	52.2–59.0		
M3a	Lat: 17.12 Long: 78.42	Pink, fine-grained monzo-granite	50.7		Leucocratic Granite
M3b		Weathered equivalent of M3a, from dug well at 2 m depth	51.6		
M7a	Lat: 17.12 Long: 78.42	Grey, fine-grained syeno-granite (outcrop sample)	51.7		Leucocratic Granite
M7b		Weathered equivalent of M7a	54.8		
M4a	Lat: 17.16 Long: 78.41	Amphibole-bearing monzo-granite	46.6		Intermediate Granite
M4b		Weathered equivalent of M4a, from dug well at 2 m depth	nd	Archaen, Peninsular Granite complex (PGC)	
Andhra Pradesh, Waipally					
W1a	Lat: 16.98 Long: 78.89	Porphyritic monzo-granite (outcrop sample), light weathering evident	49.8		
W1b		Thoroughly weathered equivalent of W1a	52.6		
W2a	Lat: 16.98 Long: 78.89	Porphyritic granodiorite (outcrop samples)	nd		PGC, undifferentiated
W2c		Thoroughly weathered equivalent of W2a	nd		
W14a	Lat: 17.07 Long: 78.91	Pink-grey granodiorite (outcrop sample), light weathering evident	nd		
W14b		Thoroughly weathered equivalent of W14a	nd		
W16a	Lat: 17.06 Long: 78.89	Grey phaneritic biotite granodiorite (outcrop sample)	50.5		
W16b	Lat: 17.05 Long: 78.89	Grey granodiorite, thoroughly weathered, adjacent dug well close to W16a, in situ depth unknown	53.1		
Sri Lanka, Plonnaruwa					
P1a	Lat:7.98 Long:81.00	Charnockitic gneiss	nd		
P1b		Slight to moderately weathered equivalent of P1a	nd		
P2a	Lat:7.97 Long: 80.99	Charnockitic gneiss	nd	Archaen, Highland Complex	
P2b		Slight to moderately weathered equivalent of P2a	nd		
P3a	Lat: 7.97 Long:80.99	Chanockitic gneiss	nd		
P3b		Slight to moderately weathered equivalent of P3a	nd		

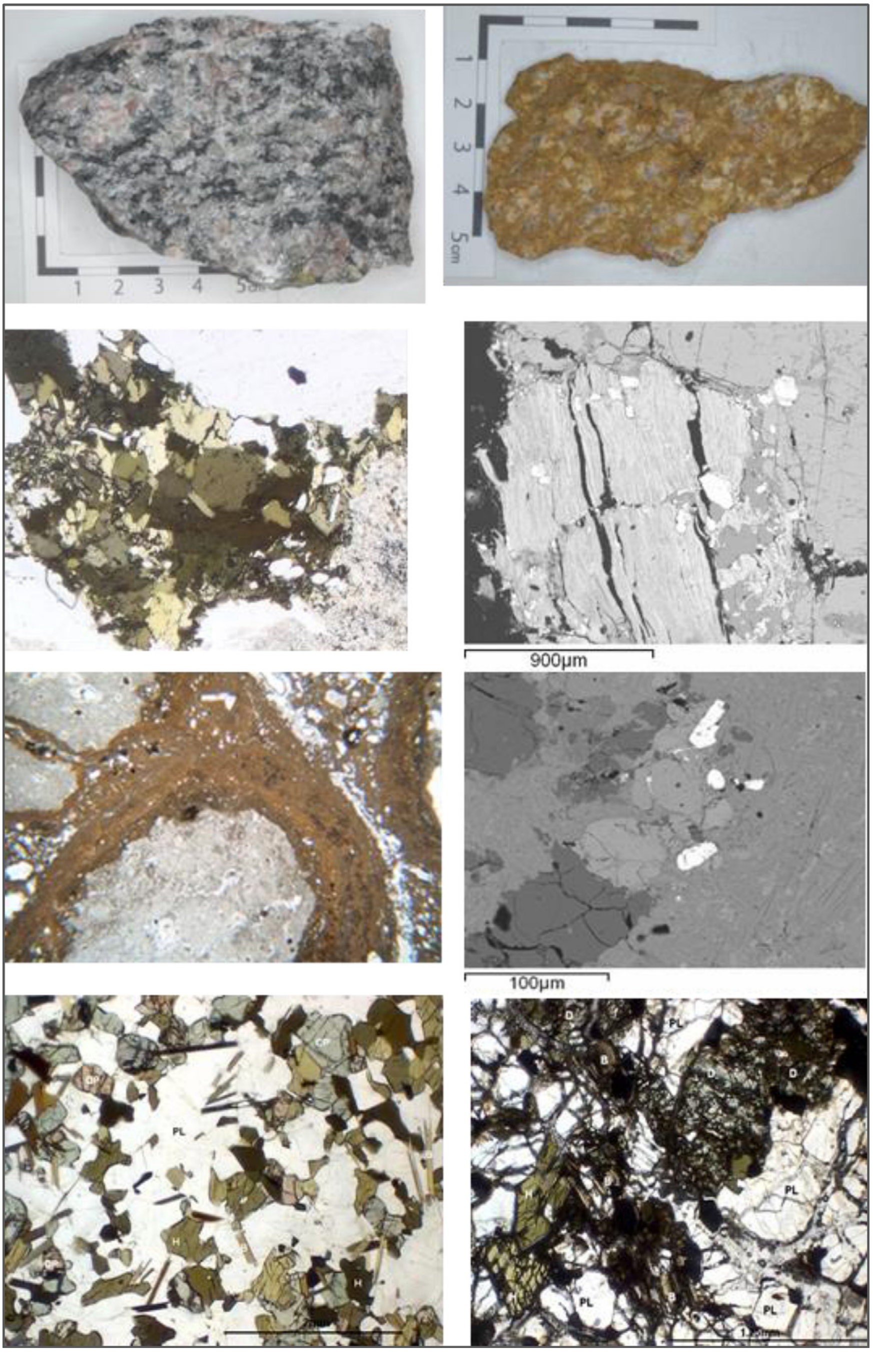

Fig. 2. Photomicrographs and EM-EBSD images of bedrock and regolith lithologies from the study sites. Top: Maheshwaram, M2 (L) bedrock, (R) regolith, in hand specimen; Upper middle: Maheshwaram, (L) M2a photomicrograph, plane polarised light, magnification 10×, (R) M2b EM-EBSD image; Lower middle: Waipally, (L) calcrete WC photomicrograph, magnification 2×, (R) W2c EM-EBSD image; Bottom: Plonnaruwa, charnockitic gneiss under PPL (L) bedrock, (R) regolith.

Table 2
Abundance and F content of F-bearing crystalline mineral phases, Maheshwaram, Andhra Pradesh.

	Mineral abundance (%) by petrographic observation									
	Fresh rock					Weathered rock				
	2 A	3A	4A	7A	Average across sites	2B	3B	4B	7B	Average across sites
Fluorite	0	0.16	0	0	0.04	0	0	0	0	0.00
Apatite	1.2	0.24	0.3	0.05	0.45	0.3	0	0	0.05	0.09
Biotite	24	1.52	3.4	1.30	7.56	7.4	3.1	0.8	3.45	3.69
Amphibole	0	0	7.4	0	1.85	0	0	0	0	0.00
Titanite	0.2	0.02	0.2	0.05	0.12	0.4	0	0	0	0.10
Epidote	2	0.24	0.7	0.3	0.81	0.7	0.1	0.4	1.10	0.58
Chlorite	4.7	1.68	0.8	0.10	1.82	1.6	0	0	0.29	0.47
Calcite	0	0	0	0	0.00	0.5	2.4	44.6	0	11.88

	Mineral F content, as weight %									
	Fresh rock					Weathered rock				
	2A	3A	4A	7A	Average across sites	2B	3B	4B	7B	Average across sites
Fluorite	na	31.57	na	na	31.57	na	na	na	na	–
Apatite	3.48	3.36	2.36	3.45	3.16	2.4	na	na	3.06	2.73
Biotite	0.16	0.29	0.52	0.09	0.27	0	0.05	0.03	0.03	0.03
Amphibole	na	na	0.24	na	0.24	na	na	na	na	–
Titanite	0.49	0.88	0.29	0.71	0.59	0.3	na	na	na	0.30
Epidote	0	1.06	1.17	0.02	0.56	0	0	0.16	0	0.04
Chlorite	0	0	0	0.01	0.00	0	na	na	0.01	0.01
Calcite	na	na	na	na	–	nd	nd	nd	na	nd

	Component mineral contribution to whole rock F content, wt %											
	Fresh rock						Weathered rock					
	2A	3A	4A	7A	Average across sites	Fraction of total F	2B	3B	4B	7B	Average across sites	Fraction of total F
Fluorite		0.0505			0.0126	0.25					0.0000	
Apatite	0.0418	0.0081	0.0071	0.0017	0.0147	0.29	0.0072			0.0015	0.0022	0.65
Biotite	0.0384	0.0044	0.0177	0.0012	0.0154	0.31	0.0000	0.0016	0.0002	0.0010	0.0007	0.21
Amphibole			0.0178		0.0044	0.09					0.0000	
Titanite	0.0010	0.0002	0.0006	0.0004	0.0005	0.01	0.0012				0.0003	0.09
Epidote	0.0000	0.0025	0.0082	0.0001	0.0027	0.05	0.0000	0.0000	0.0006	0.0000	0.0002	0.05
Chlorite	0.0000	0.0000	0.0000	0.0000	0.0000		0.0000			0.0000	0.0000	
Calcite					0.0000		nd	nd	nd			
Whole rock F, wt %	0.0811	0.0657	0.0513	0.0033	0.0504		0.00840	0.00155	0.00088	0.00259	0.00336	
Whole rock F, ppm	811	657	513	33	504		84	16	9	26	34	
Fraction F lost on weathering	0.90	0.98	0.98	0.22	0.77							

na: not available; nd: not determined.

Table 3
Abundance and F content of F-bearing crystalline mineral phases, Waipally, Andhra Pradesh.

	Mineral abundance (%) by petrographic observation												
	Fresh rock						Weathered rock						
	1A	2A	14A	16A	17A	Average across sites	1B	2C	14B	16B	17X	Average across sites	W-Calcrete
Fluorite	0.1	0	0.05	0	0	0.03	0	0	0	0	0	0.00	0
Apatite	0.9	0.5	0	0.57	0	0.39	0.2	0.46	0.1	0.2	0.30	0.25	0.1
Biotite	0	1.2	1.6	4.92	0.03	1.55	2.3	5.37	2.4	2.05	2.80	2.98	0.05
Amphibole	0	0	0	0	0	0.00	0	0	0	0	0	0.00	0
Titanite	1.9	2.6	0.6	0	0	1.02	0.4	0.28	0.2	0.05	0.70	0.33	0.05
Epidote	0.4	1.4	0.6	1.13	4.58	1.62	0.1	1.11	0.6	0.1	14.40	3.26	0
Chlorite	5.3	9	1	1.61	0.06	3.39	0	1.76	1.1	3.91	1.70	1.69	0.05
Calcite	0	0	0	0	0	0.00	0	0	0	0	0	0.00	91.8

	Mineral F content, as weight %												
	Fresh rock						Weathered rock						
	1A	2A	14A	16A	17A	Average where present	1B	2C	14B	16B	17X	Average across sites	W-Calcrete
Fluorite	27.36	na	22.24	na	na	24.80	na	na	na	na	na	–	na
Apatite	2.66	3.09	na	2.64	na	2.80	2.83	2.86	3.25	2.32	2.95	2.84	2.76
Biotite	na	0.18	0.33	0.24	0.03	0.20	0	0	0.24	0	0.03	0.05	0.13
Amphibole	na	na	na	na	na	–	na	na	na	na	na	–	na
Titanite	1.15	0.74	0.69	na	na	0.86	1.28	1.03	0.65	0.14	0.45	0.71	0.92
Epidote	0.01	1.1	0	0.45	0.011	0.31	1.01	0	0.43	1.01	0	0.49	na
Chlorite	0	0.01	0	0.02	0.00	0.01	na	0	0.01	0	0	0.00	0.06
Calcite	na	na	na	na	na	–	na	na	na	na	na	–	0.02

	Component mineral contribution to whole rock F content, wt%														
	Fresh rock							Weathered rock							
	1A	2A	14A	16A	17A	Average across sites 1,2,14,16	Fraction of total F	1B	2C	14B	16B	17X	Average across sites 1,2,14,16	Fraction of total F	W-Calcrete
Fluorite	0.0274		0.0111			0.0096	0.21						0.0000		0.0000
Apatite	0.0239	0.0155		0.0150		0.0136	0.30	0.0057	0.0132	0.0033	0.0046	0.01	0.0067	0.57	0.0028
Biotite		0.0022	0.0053	0.0118	0.0000	0.0048	0.11	0	0	0.0058	0	0.00	0.0014	0.12	0.0001
Amphibole						0.0000							0.0000		0.0000
Titanite	0.0219	0.0192	0.0041			0.0113	0.25	0.0051	0.0029	0.0013	0.0001	0.00	0.0023	0.20	0.0005
Epidote	0.0000	0.0154	0.0000	0.0051	0.0005	0.0051	0.11	0.0010	0	0.0026	0.0010	0.00	0.0012	0.10	0.0000
Chlorite	0.0000	0.0009	0.0000	0.0003	0.0000	0.0003			0	0.0001	0	0.00	0.0000		0.0000
Calcite															0.0184
Whole rock F, wt %	0.0732	0.0532	0.0205	0.0323	0.0005	0.0448		0.0118	0.0160	0.0130	0.0057	0.0128	0.0116		0.0217
Whole rock F, ppm	732	532	205	323	5	448		118	160	130	57	128	116		217
Fraction F lost on weathering	0.84	0.70	0.37	0.82		0.68									

na: not available.

Table 4
Abundance and F content of F-bearing crystalline mineral phases, Plonnaruwa, Sri Lanka.

	Mineral abundance (%) by petrographic observation							
	Fresh rock				Weathered rock			
	P1	P2	P3	Average across sites	P1	P2	P3	Average across sites
Apatite	0.75	0.2	0.5	0.48	0.5	0.1	0.1	0.23
Biotite	8	0	3	3.67	0	0	5	1.67
Titanite	0	10	0	3.33	8	1	0	3.00
Amphibole	40	20	15	25.00	0	30	0	10.00

	Mineral F content, as weight %							
	Fresh rock				Weathered rock			
	P1	P2	P3	Average across sites	P1	P2	P3	Average across sites
Apatite	2.79	2.57	2.68	2.68	2.16	2.16	2.16	2.16
Biotite	0.42	0	0.32	0.25	na	na	0.32	0.32
Titanite	na	0.37	na	0.37	0.26	0.26	na	0.26
Amphibole	0.24	0.21	0.225	0.23	na	0.17	na	0.17

	Component mineral contribution to whole rock F content, wt %									
	Fresh rock					Weathered rock				
	P1	P2	P3	Average across sites	Fraction of total F	P1	P2	P3	Average across sites	Fraction of total F
Apatite	0.0209	0.0051	0.0134	0.0132	0.14	0.0108	0.0022	0.0022	0.0050	0.14
Biotite	0.0336	0.0000	0.0096	0.0144	0.15			0.0160	0.0053	0.15
Titanite		0.0370		0.0123	0.13	0.0208	0.0026		0.0078	0.22
Amphibole	0.0960	0.0420	0.0338	0.0573	0.59		0.0510		0.0170	0.48
Whole rock F, wt %	0.1505	0.0841	0.0568	0.0971		0.0316	0.0558	0.0182	0.0352	
Whole rock F, ppm	1505	841	568	971		316	558	182	352	
Fraction F lost on weathering	0.79	0.34	0.68	0.60						

na: not available.

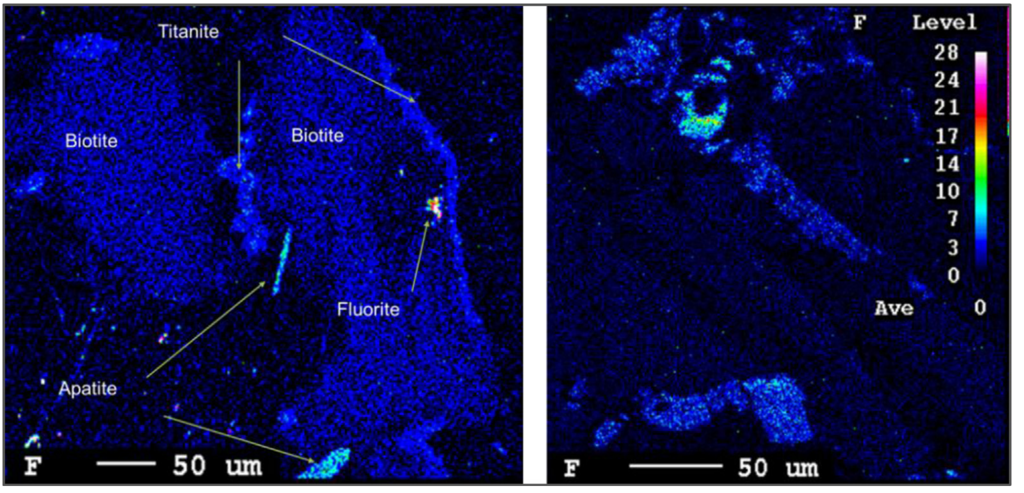

Fig. 3. EM-EDX image showing F occurrence in biotite, titanite, apatite and fluorite, Maheshwaram bedrock sample M3a. The colour scaling is relative, from the lowest F content as indicated for biotite, the intermediate brighter blue indicating a moderate F content in titanite rimming biotite, the brighter light blue indicating higher F content in apatite, and the reds and pinks indicating the highest F content in fluorite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

F contents are summarised in Table 5. Individual mineral contributions to F removal as a consequence of the bedrock to regolith weathering are itemised in Table 6.

4.1. Mineralogy of the bedrock and regolith

Petrological classification of the fresh bedrock granites, granodiorites and granitic gneisses of the Peninsular Granite Complex in Andhra Pradesh (Maheshwaram, Waipally) and the Highland Complex in Sri Lanka (Plonnaruwa) is indicated in Table 1. All the bedrock samples contained quartz, alkali feldspar and plagioclase feldspar as major components. Biotite was also ubiquitous but at less than 10% abundance except in the porphyritic biotite granodiorite of the Biotite Granite unit at Maheshwaram where its abundance is 24%. At Maheshwaram, amphibole is present only in the amphibole-bearing monzo-granite of the Intermediate Granite unit (at 7.4% abundance), and at Waipally only in sparse

Table 5
Summary of mineral F contents: average bedrock mineral F contents, and previously published ranges, mass %.

Mineral	Formula	Published	Maheshwaram	Waipally	Waipally mafic vein	Plonnaruwa
[a]Amphiboles	$Ca_2(Mg,Fe)_4Al[Si_7AlO_{22}](OH)_2$	0–2.69 *0.027–2.9*	0.24	0.2	0.42	0.23
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	0.16–5.60 *1.35–2.56*	3.16	2.75	2.04	2.68
Biotite	$K_2(Mg,Fe)_4(Fe,Al)_2[Si_6Al_2O_{20}](OH)_2(F,Cl)_2$	0–0.91 *0.095–3.5*	0.27	0.25	0.91	0.25
[b]Chlorite	$(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$	Not available	0.03	0.02	–	–
[c]Epidote	$Ca_2(Fe^{3+},Al)Al_2O{\cdot}OH{\cdot}Si_2O_7{\cdot}SiO_4$	Not available	0.01, 1.13	0.01, 0.99	0.02	–
Fluorite	CaF_2	*51.33*	31.57	26.33	–	–
Titanite	$CaTi[SiO_4](O,OH,F)$	0.61	0.53	0.79	–	0.37

[a] Magnesio-hornblende.
[b] Ripidolite.
[c] Two varieties of epidote are noted – indicates not present.
Values in italics from Correns (1956). Other published values from Deer et al. (1992).

Table 6
Mineral contributions to F removal as a consequence of the bedrock to regolith weathering.

	Mineral contributions to weathering F removal, wt%					Mineral contributions to weathering F removal, fraction					Fraction of bedrock F
	2A	3A	4A	7A	Average across sites	2A	3A	4A	7A	Average across sites	
Andhra Pradesh, Maheshwaram											
Fluorite		0.0505			0.0126		0.79			0.20	0.25
Apatite	0.0346	0.0081	0.0071	0.0002	0.0125	0.48	0.13	0.14	0.27	0.25	0.29
Biotite	0.0384	0.0029	0.0174	0.0001	0.0147	0.53	0.04	0.35	0.19	0.28	0.31
Amphibole			0.0178		0.0044			0.35		0.09	0.09
Titanite	−0.0002	0.0002	0.0006	0.0004	0.0002	0.00	0.00	0.01	0.49	0.13	0.01
Epidote	0.0000	0.0025	0.0076	0.0001	0.0025	0.00	0.04	0.15	0.08	0.07	0.05
Chlorite				−0.00002					−0.03	−0.01	
F removed on weathering, wt %	0.0727	0.0642	0.0504	0.00073	0.0470	1.00	1.00	1.00	1.00	1.00	

	Mineral contributions to weathering F removal, wt %					Mineral contributions to weathering F removal, fraction					Fraction of bedrock F
	1A	2A	14A	16A	Average across sites	1A	2A	14A	16A	Average across sites	
Andhra Pradesh, Waipally											
Fluorite	0.02736		0.01112		0.010	0.45		1.47		0.48	0.21
Apatite	0.01828	0.002294	−0.00325	0.010408	0.007	0.30	0.06	−0.43	0.39	0.08	0.30
Biotite		0.00216	−0.00048	0.011808	0.003		0.06	−0.06	0.44	0.11	0.11
Titanite	0.01673	0.016356	0.00284	−0.00007	0.009	0.27	0.44	0.38	0.00	0.27	0.25
Epidote	−0.00097	0.0154	−0.00258	0.004075	0.004	−0.02	0.41	−0.34	0.15	0.05	0.11
Chlorite	0	0.0009	−0.00011	0.000322	0.000		0.02	−0.01	0.01	0.01	
F removed on weathering, wt %	0.0614	0.03711	0.00754	0.026543	0.027	1.00	1.00	1.00	1.00	1.00	

	Mineral contributions to weathering F removal, wt %				Mineral contributions to weathering F removal, fraction				Fraction of bedrock F
	P1	P2	P3	Avg across sites	P1	P2	P3	Avg across sites	
Sri Lanka, Plonnaruwa									
Apatite	0.010	0.003	0.011	0.008	0.09	0.11	0.29	0.16	0.14
Biotite	0.034	0.000	−0.006	0.009	0.28	0.00	−0.17	0.04	0.15
Titanite	−0.021	0.034	0.000	0.005	−0.17	1.21	0.00	0.35	0.13
Amphibole	0.096	−0.009	0.034	0.040	0.81	−0.32	0.87	0.45	0.59
F removed on weathering, wt %	0.119	0.028	0.039	0.062	1.00	1.00	1.00	1.00	

mafic veins observed in the field. By contrast, hornblende amphibole is a major component of charnockitic gneiss (15–40% abundance) throughout the Highland Complex in Sri Lanka. Apatite is ubiquitous, though minor at around 1% abundance in all three catchments. Epidote is ubiquitous at Maheshwaram and Waipally, at maximum 2% abundance though locally higher. Titanite is also very common, almost ubiquitous, throughout the Peninsular Granite complex at Maheshwaram and Waipally, sometimes as a primary mineral but normally as a secondary phase associated with biotite; it is less common in the Highland Complex in Sri Lanka despite occasionally reaching 10% abundance. Fluorite is occasionally present (i.e. in three of eight bedrock samples) at Maheshwaram and Waipally, at a maximum abundance of 0.16%, but is absent at Plonnaruwa. Chlorite is commonly present, at 0.1–9% abundance, in the Peninsular Granite, apparently as a retrograde alteration product of biotite and other ferro-magnesian minerals; sericite is similarly present as an early alteration product of plagioclase feldspar. None of the bedrock samples exhibited more than light weathering, however, with their chemical alteration index (CIA) values (Nesbitt and Young, 1989) ranging between 46.6 and 51.7 (Table 1). Calcite was not observed in any bedrock samples.

In the regolith, a coarse-grained, friable texture and ochre colouration are visual evidence of pervasive weathering; regolith CIA values are uniformly greater than their bedrock equivalents, ranging between 51.6 and 59.0 (Table 1). X-ray Diffraction indicates the general pattern of weathering to include partial destruction but not total elimination of potassium feldspar and biotite, and an increase in clay alteration products and iron oxyhydroxides. Remnant feldspars in the regolith are commonly fractured and with extensive sericitic alteration. Biotite is much reduced, and the remnant biotite and chlorite crystals are fragmented, with Fe oxyhydroxide deposits along the remnant crystal cleavages. Apatite and titanite persist in the regolith, generally at lesser abundances than in bedrock. Fluorite is absent. Calcite occurs as an authigenic phase in the Maheshwaram regolith (Fig. 2), at very variable abundance, 0.5–45%, and as widespread calcrete present as fracture-filling layers several centimetres thick throughout the Waipally catchment. The Waipally calcrete has a banded calcite matrix enclosing numerous small clasts of quartz, feldspar and occasional epidote, biotite, zircon and titanite (Fig. 2).

4.2. F-bearing crystalline phases in the bedrock and regolith, and cumulative F content

The eight crystalline mineral phases identified as containing F, determined by electron microprobe EM-EDX analysis (Fig. 3, Tables 2–4) are fluorite, apatite, biotite, amphibole, titanite, epidote, chlorite, and calcite. Of these, all but calcite and fluorite were present in some or all samples from the bedrock and the regolith. Calcite was not observed in any bedrock samples, and fluorite was not observed in any regolith samples. The mineralogical F contents at Maheshwaram, Waipally and Plonnaruwa are consistent with ranges previously published for individual minerals (Table 5).

The total F content of the Pre-Cambrian bedrock, as the cumulative F determined within crystalline mineral phases and averaged over the sampled lithologies, is 504 ppm (range 33–811 ppm) at Maheshwaram, 408 ppm (range 205–732 ppm) at Waipally, and 971 ppm (range 568–1505 ppm) at Plonnaruwa, consistent with previously published ranges for granitic rocks (Jeffery and Hutchinson, 1986). The ranges of values within equivalent mapped units indicates spatial variability in F content at the scale of 0.1 m, the approximate sample size, but the sampling frequency is insufficient to generalise on the range of F content in specific lithologies present. The ranges in F content here assigned to bedrock may also be influenced to an extent by the effects of early stage chemical alteration, and further work with rock cores taken at depths well beyond the fractured layer at the base of the regolith would be required to demonstrate this. Equivalent, cumulative and averaged regolith F contents are 34 ppm (Maheshwaram), 116 ppm (Waipally) and 352 ppm (Plonnaruwa). Weathering of the primary bedrock consistently leads to depletion of F in the remnant regolith, notwithstanding the partial accumulation of F in calcrete (Table 3) and potentially also in amorphous authigenic phases not determined here.

In the bedrock, apatite (hosting >100 ppm F averaged over the sampled lithologies) is the sole principal F-bearing crystalline mineral phase common to all three catchments, but there is no common dominant mineral phase (hosting >20% of the total F averaged over the sampled lithologies). At Maheshwaram, biotite and fluorite join apatite as principal F hosts; amphibole and epidote are subsidiary hosts (with 10–100 ppm F) and titanite is minor (<10 ppm). The dominant Maheshwaram hosts are, in decreasing order, biotite, apatite and fluorite. At Waipally, titanite and fluorite join apatite as principal F hosts; biotite and epidote are subsidiary hosts, and chlorite is minor. The dominant Waipally hosts, in decreasing order, are apatite, titanite and fluorite. At Plonnaruwa, apatite, biotite, titanite and the amphibole hornblende are all principal F hosts in the bedrock, with hornblende dominating, contributing nearly 60% of the total F.

In the regolith, partial or total destruction of the primary bedrock minerals and consistent depletion of F in the remnant minerals has resulted in a much reduced total F content. Only at Plonnaruwa does an individual mineral persist as a principal F host in the regolith (as defined above), with hornblende hosting 170 ppm F on average across the sampled regolith lithologies. Fluorite is absent from the regolith in all catchments. Apatite and biotite are much reduced as F hosts but persist as the dominant F-bearing crystalline mineral phases at Maheshwaram, with remnant apatite and titanite persisting as the dominant F hosts at Waipally. At Maheshwaram, titanite and epidote remain as minor, though depleted F hosts in the regolith. Similarly at Waipally, biotite and epidote are depleted but remain as minor F hosts. At Plonnaruwa, amphibole hosts nearly 50% of the total F in the regolith, and titanite persists sufficiently to remain as an additional principal F host.

Implications of these determinations for the mineral-specific contributions to F mobilisation during bedrock weathering are discussed in Section 5.2 below.

4.3. Leaching experiments and regolith profiles

Leaching experiments indicate the relative availability of F to infiltrating groundwater from the bedrock and regolith. Leachates remained under-saturated with respect to fluorite throughout. At an early stage (1–3 h) F^- is leached at higher concentration from the regolith samples than from bedrock samples in six of the nine bedrock–regolith pairs investigated (Fig. 4). This is despite the lower crystalline phase cumulative F content of the regolith samples compared to bedrock samples in all nine cases (Tables 2–4). Leachate from the Maheshwaram M2 regolith consistently exceeds that from bedrock in the longer term also, up to 5000 h (Fig. 4), and throughout the Maheshwaram M2 regolith profile to 500 h, where the F content is also consistently lower in the regolith than the bedrock (Fig. 5). Note however that there is no consistent leachate trend with depth in either of the profiles from Waipally and Plonnaruwa. At least a proportion of leached F is likely to be desorbed from sites associated with amorphous or cryptocrystalline phases and is therefore not directly related, and is in part additional to, the crystalline mineral sources determined in the mineral mass balance for F. This imbalance would likely be greater in the regolith than the bedrock.

5. Discussion

5.1. Mineral F sources, availability of F^- to groundwater and the significance of the regolith

The mass balances for F (Tables 2–4 and Section 4.2 above) directly quantify the F-bearing crystalline mineral phases, demonstrating the potential, present day, geological sources of groundwater F^- at the three study sites. Of the eight mineral sources identified, three (apatite, biotite, titanite) are present in the bedrock and persist in the regolith in all three catchments. Apatite is uniquely ubiquitous as a principal F-bearing phase (>100 ppm F) in bedrock, with other common principal F hosts being biotite, titanite, fluorite and amphibole. Apatite is dominant (contributing >20% of the total) along with fluorite and either biotite (Maheshwaram) or titanite (Waipally) in the Peninsular Granite complex of Andhra Pradesh. The amphibole hornblende is the dominant host for F in both bedrock and regolith at Plonnaruwa in Sri Lanka. Fluorite, apparently as a primary mineral, is a principal and dominant F host in the Peninsular Granite bedrock but is less commonly present than apatite, biotite and titanite, was not observed at Plonnaruwa and is absent from the regolith in all catchments. The primary mineral phases that do persist in the regolith are much reduced in their F content; only hornblende amphibole, at Plonnaruwa, persists as a principal phase. Throughout the regolith, however, apatite, biotite and titanite remain more generally significant, and calcite becomes a principal host for F in the Waipally catchment where it is abundant as discrete layers of calcrete, in part on account of entrained residual primary minerals (Table 3).

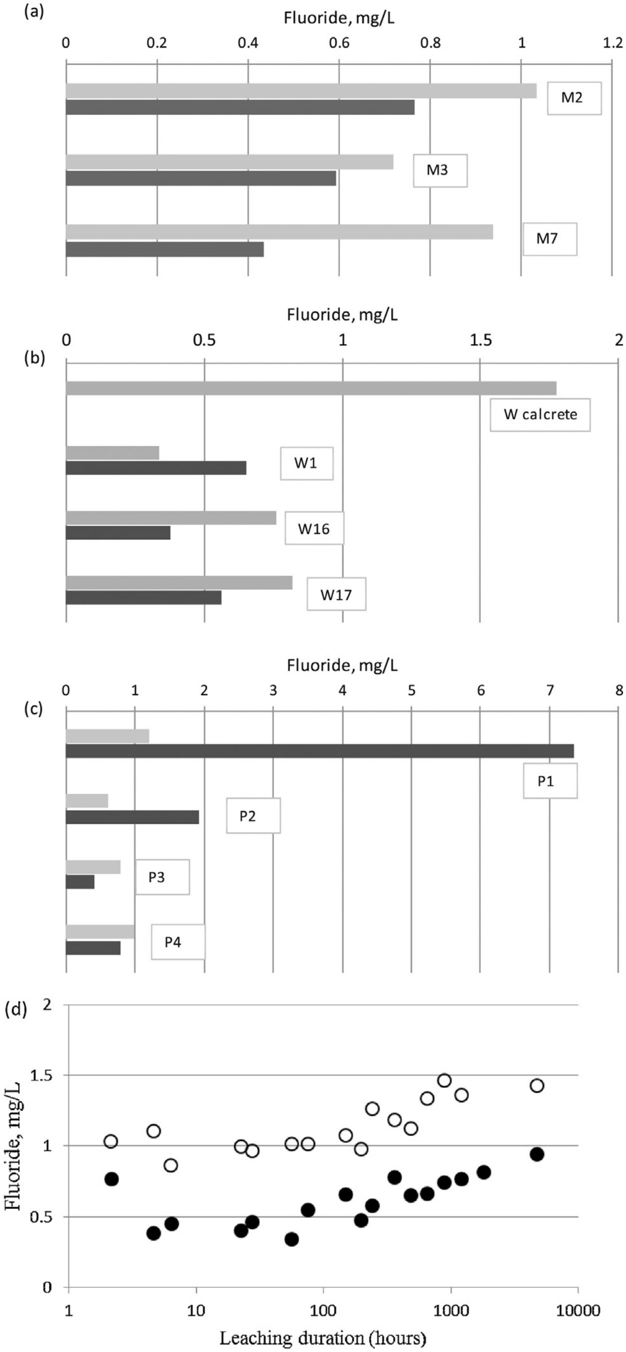

Fig. 4. Leachate [F⁻] from powdered regolith (light grey) and bedrock (dark grey) samples of the Peninsular Granite complex, (a) from Maheshwaram at 2 h leaching (b) from Waipally at 2 h leaching, (c) from Plonnaruwa at 3 h leaching, and (d) evolution of leachate [F⁻] with time for Maheshwaram biotite granite and regolith, site M2. Note that at Waipally the two W17 samples are not lithological equivalents and the pedogenic calcrete does not have a bedrock equivalent.

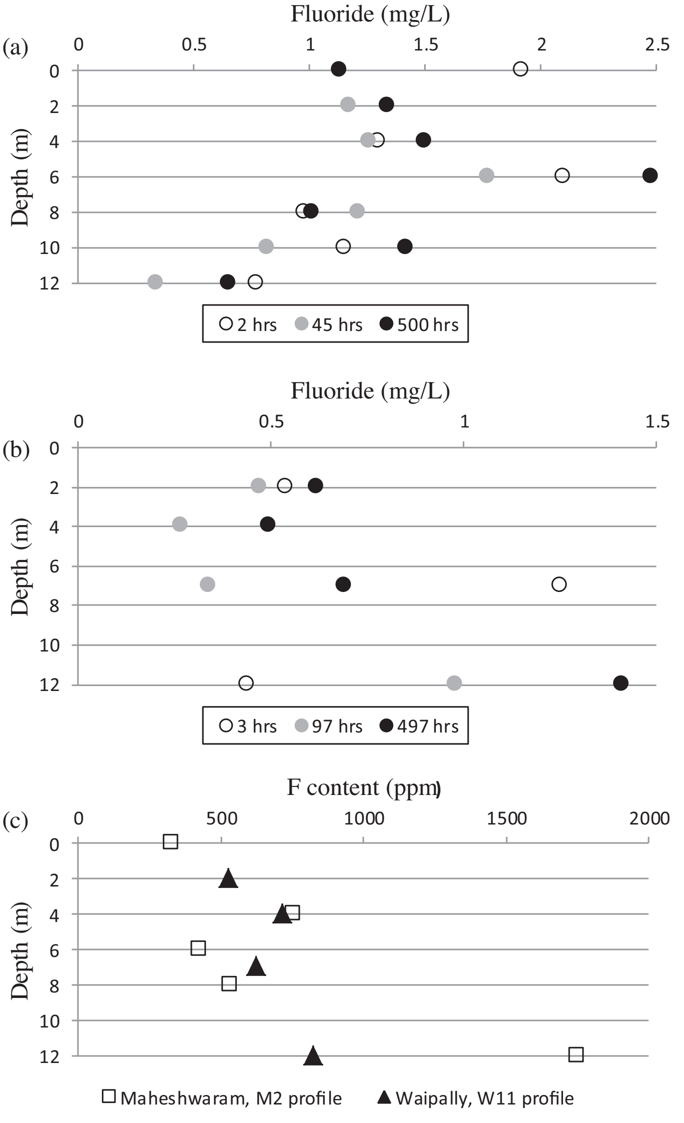

Fig. 5. Leachate [F⁻] from regolith samples in depth profile from the Peninsular Granite complex, (a) Maheshwaram and (b) Waipally; and (c) F content of profile samples.

Abundance of F is not a straightforward indicator of availability of F^- to groundwater. Leaching experiments are strongly indicative of the relative strength of regolith material in general as a source of groundwater F^-, irrespective of the greater F content of bedrock (Figs. 4 and 5). The release of F from primary minerals in bedrock as part of the weathering process has likely been accompanied by partial sequestering of F^- within amorphous and other authigenic phases from which it may be released with relative ease. Secondary oxides of iron and aluminium, and authigenic clays are ubiquitous throughout the regolith (Hallett, 2012) and likely provide the dominant sites for sorption/desorption reactions to occur. In addition, the high porosity of the regolith compared to the bedrock (Dewandel et al., 2006) provides an enhanced mineral surface area for water–rock interaction, including sorption/desorption and hence a greater potential for release of F. The leaching observations do not disprove the bedrock

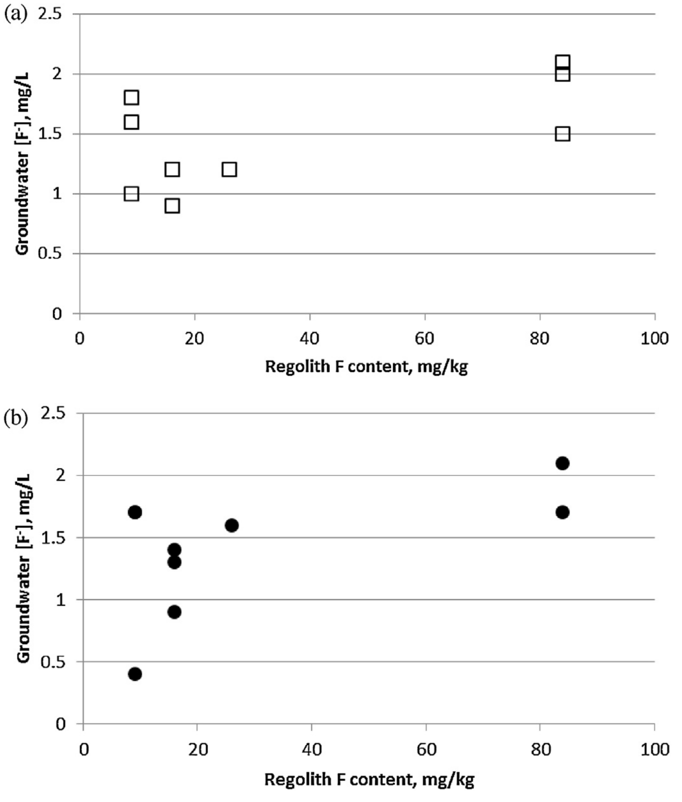

Fig. 6. Groundwater [F^-] *v* regolith F content, Maheshwaram; (a) pre-monsoon, (b) post-monsoon.

as a source of F^- to groundwater in the present day, but they emphasize the likely significance of the regolith as a major influence on groundwater [F^-] and its seasonal variability, consistent with the suggestion (Sreedevi et al., 2006) that groundwater [F^-] rises following groundwater recharge.

At Maheshwaram, where groundwater [F^-] has been determined at or very close to the sites of the rock sample locations (Sreedevi et al., 2006; Atal, 2008), the mass balance and leaching results allow further investigation of factors controlling groundwater [F^-]. It is commonly stated that spatial variation in groundwater [F^-] is linked to spatial variability in F content of the aquifer material (e.g. Reddy et al., 2010). At Maheshwaram, bedrock F content and groundwater [F^-] are unrelated, but a weak positive correlation is evident for the regolith under both pre- and post-monsoon conditions (Fig. 6). Correlation of groundwater [F^-] and leachate [F^-] for regolith and bedrock (Fig. 7) provides a positive test for the significance of the regolith.

Results emphasise the significance, and possible dominance, of the regolith as a source of groundwater F^- in the Archaen bedrock/regolith aquifer of peninsular India and Sri Lanka. They provide a cautionary perspective on schemes of managed aquifer recharge which postulate dilution of [F^-] by enhanced recharge but which risk the opposite, by mobilising additional F to groundwater. Such schemes should always include monitoring of [F^-] in profile at the recharge sites prior to and during implementation, and monitoring thereafter.

5.2. Mineral specific F mobilisation during bedrock weathering

The bedrock–regolith mass balances for F also indicate directly the cumulative mineral contributions to flux of F during past weathering (Table 6). Present day groundwater [F^-] is however unrelated

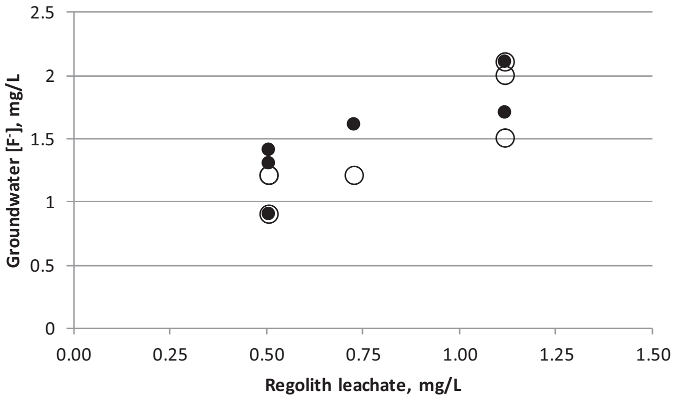

Fig. 7. Groundwater [F^-] *v* experimental leachate [F^-] from regolith, Maheshwaram. Open circles: pre-monsoon; filled circles: post-monsoon.

to this historical flux of F. Unsurprisingly, the patterns of weathering change with time as the nature of the weathering substrate evolves, i.e. as the regolith evolves through its complex, likely multiphase (Dewandel et al., 2006) weathering history. Also, comparison of the mineral contributions to past F flux (Table 6) and to bedrock F (Tables 2–4) demonstrates the extent of incongruence of the weathering process. At Maheshwaram, biotite (28%), apatite (25%) and fluorite (20%) were the dominant sources releasing F^- during weathering, in approximate congruence with their contribution to bedrock F content (31%, 29% and 25% respectively); only titanite, a minor mineral host for F in the bedrock, contributed to the release of F in excess of its abundance. But at Waipally, fluorite, one of the principal hosts for F in bedrock, has contributed a disproportionately large fraction of F released during weathering, whereas apatite has been recalcitrant. In the amphibole-rich charnockitic gneiss at Plonnaruwa, amphibole is the dominant source of F^- released during weathering and titanite, here a principal mineral host for F in the bedrock, has contributed in excess of its abundance as at Maheshwaram. These distinctions between the relative mineralogical abundance of F in bedrock and the mineral contributors to release of F during bedrock weathering indicate in part the transience of mineral F distribution over the course of weathering and in part the distinction between mineralogical F content and F availability.

5.3. An estimate of weathering duration

With the mass balances of F demonstrating the flux of F as a consequence of weathering (Table 6), it is of interest to estimate the duration of weathering responsible for the in situ regolith. A first estimate can be made in principal by linking the weathering flux of F to estimates of flux of groundwater through the bedrock–regolith aquifer, taking recharge rate as a representation of groundwater flux. In addition to the pre-requisite that the samples are themselves representative of the fresh bedrock and regolith, as described and discussed above, this approach makes three simplifying assumptions: weathering is iso-volumetric, groundwater [F^-] is maintained at an equilibrium state, and current climatic conditions are representative of average conditions over the estimated duration of weathering calculated. Within these constraints, the duration of weathering responsible for the in-situ regolith has been estimated (Table 7) for Maheshwaram at the three points where bedrock/regolith pairs are coincident with points of measured groundwater [F^-]. The resultant range of weathering durations responsible for the preserved regolith in Andhra Pradesh is 250–380 Ka, close to the value of 223 Ka estimated from denudation rates elsewhere in southern India (Gunnell, 1998). This will be an underestimate of the true weathering duration if incipient weathering in the samples taken as representing fresh bedrock has been effective in mobilising F. The estimate addresses cumulative weathering duration rather than the true age or the age sequence of weathering. Therefore it is not directly comparable to the multiphase dating of weathering, Jurassic to Quaternary, proposed by Dewandel et al. (2006), and the

Table 7
Duration of weathering, for in situ regolith, Maheshwaram.

	M2	M3	M4
Bedrock F content, mg/kg	812	657	513
Regolith F content, mg/kg	84	15	9
F removed by weathering, mg/kg	728	642	504
Groundwater F content, mg/L	1.88	1.13	1.36
Groundwater volume for weathering, as effective depth (mm)	1.04E+07	1.53E+07	1.00E+07
Weathering duration, years	2.57E+05	3.78E+05	2.47E+05

Annual rainfall taken as 812 mm, and recharge is 5% of annual rainfall (Chand et al., 2005); density of granitic gneiss taken as 2700 kg/m^3; observed regolith thickness is 10 m.

profiles of regolith F content (Fig. 5) are too coarse to test the interpretation (Dewandel et al., 2006) of a two-stage regolith development.

Conflict of interest

The authors confirm that there are no known conflicts of interest to disclose.

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