Mineralogical sources of groundwater fluoride in Archaen bedrock/regolith aquifers: mass balances from the Peninsular Granite Complex, southern India

[1]Bethan HALLETT, [1]William BURGESS & [2]Eva VALSAMI-JONES

[1] Department of Earth Sciences, University College London, UK bethanhallett@hotmail.com, william.burgess@ucl.ac.uk

[2] Natural History Museum, London, UK (currently School of Geography, Earth and Environmental Sciences, University of Birmingham) e.valsamijones@bham.ac.uk

Summary

A mineralogical mass balance of fluorine (F) in the Archaen gneissic bedrock and associated regolith of Andhra Pradesh, India, has been determined by petrological, mineralogical and chemical analysis. The distribution of F across eight crystalline phases and between the bedrock and the regolith, and mineral contributions to F release during weathering and regolith development are quantified at eight sites in two catchments. Accounting for groundwater [F-], simple estimates of groundwater flux suggest that the extant regolith has developed over a period of *c.*250 - 380 Ka, during which time >70% of the original bedrock F has been removed by chemical weathering. 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.

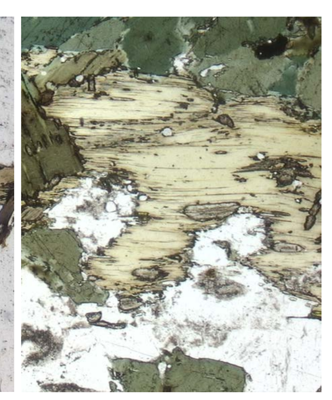
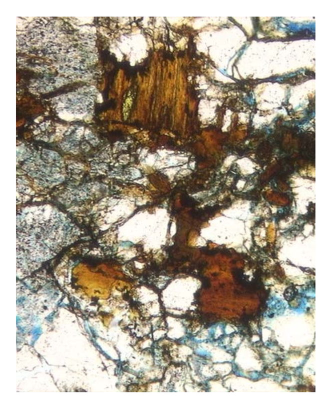
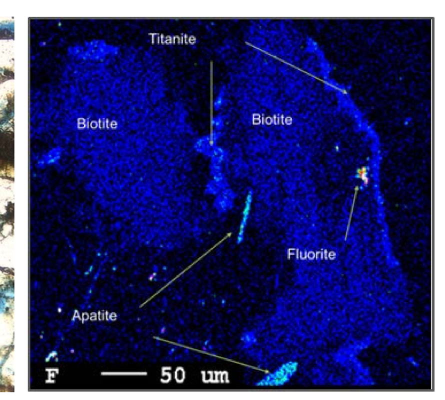
Two catchments in Andhra Pradesh, India: Maheshwaram and Waipally

In Andhra Pradesh, granitic gneisses of the Peninsular Granite Complex form the bedrock; weathered regolith mantles an irregular surface of the fractured bedrock to about 10-20 m depth (Dhakate et al. 2008). The Peninsular Granite Complex is represented in the Maheshwaram (M) catchment by Biotite Granite, Leucocratic Granite and Intermediate Granite (Geological Survey of India, 2002) and in the Wailpally (W) catchment includes younger intrusives and massive granites as well as calcrete, widely present throughout the regolith as fracture infill (Geological Survey of India, 1989). The climate is semi-arid to sub-tropical with average annual rainfall of 812 mm in Maheshwaram and 632 mm in Wailpally, most of which falls in the monsoon season. High rates of groundwater abstraction for irrigation has resulted in water table decline over the past 30 years, so that much of the regolith is now dewatered (Kumar and Ahmed 2003). Groundwater [F-] ranges from 0.40 to 4.27 mg/l in Maheshwaram (Sreedevi et al. 2006) and from 0.97 to 7.6 mg/l in Wailpally (Reddy et al. 2010). In both catchments, groundwater is under-saturated with respect to fluorite.

Methodology

From each catchment, four paired samples of fresh bedrock and associated regolith were collected from outcrop and from accessible dry dug-wells. Crystalline phase mineral abundances and F contents were determined by optical petrography, X-ray diffraction, and electron microscopy with electron backscatter detection (EM-EBSD) and energy dispersive X-ray detection (EM-EDX). Mineralogical mass balances of F in the crystalline phases of the fresh rock and weathered regolith were determined by summing the contributions of each mineral. The gross quantity of F removed during bedrock to regolith weathering was calculated by difference. The mass balances of F were used to compute the individual mineral contributions to F removal during weathering. Leaching experiments were carried out to determine the relative availability of F from the bedrock and regolith. Full analytical details are given in Hallett (2012).



Left to right: M2 bedrock, M2 regolith (hand specimens); M3 bedrock, PPL x 10 (biotite, fluorite, feldspar); M4 bedrock, PPL x 10 (biotite, hornblende, apatite); M7 regolith, PPL x 4 (biotite, epidote, feldspar); M3 bedrock, EM-EDX image showing F in biotite, titanite, apatite and fluorite.

Analytical results

The crystalline F-bearing mineral phases are: fluorite, apatite, biotite, amphibole, titanite, epidote, chlorite, and calcite. Calcite was not observed in the bedrock and fluorite was not observed in the regolith of either catchment. Mineral abundance and F content of the bedrock and regolith of Maheshwaram are tabulated (*left*) below. The dominant bedrock F hosts at Maheshwaram are, in decreasing order, biotite, apatite and fluorite. Apatite and biotite are much reduced but persist as the dominant F hosts in the regolith. The dominant bedrock F hosts at Waipally are apatite, titanite and fluorite; remnant apatite and titanite persist as the dominant F hosts in the Waipally regolith. Full analytical results are given in Hallett (2012) and Hallett et al. (*under review*).

Mineral abundance (%) by petrographic observation

	Fresh rock 2A	3A	4A	7A	Average across sites		Weathered rock 2B	3B	4B	7B	Average across sites
Fluorite	0	0.16	0	0.00	0.04		0	0	0.00	0.00	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	0.00	1.85		0	0	0	0.00	0.00
Titanite	0.2	0.02	0.2	0.05	0.12		0.4	0	0	0.00	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	0.00	0.00		0.5	2.4	44.6	0.00	11.88

Mineral F content, as weight %

	Fresh rock 2A	3A	4A	7A	Average across sites		Weathered rock 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	0.00	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 2A	3A	4A	7A	Average across sites	Fraction of total F	Weathered rock 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								

Mineral contributions to F removal as a consequence of bedrock weathering to regolith are summarised *below right*. The results demonstrate the extent of incongruence of the weathering process.

Andhra Pradesh, Maheshwaram

	Mineral contributions to weathering F removal, wt% 2A	3A	4A	7A	Average across sites	Mineral contributions to weathering F removal, fraction 2A	3A	4A	7A	Average across sites	Fraction of bedrock F
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	

Andhra Pradesh, Waipally

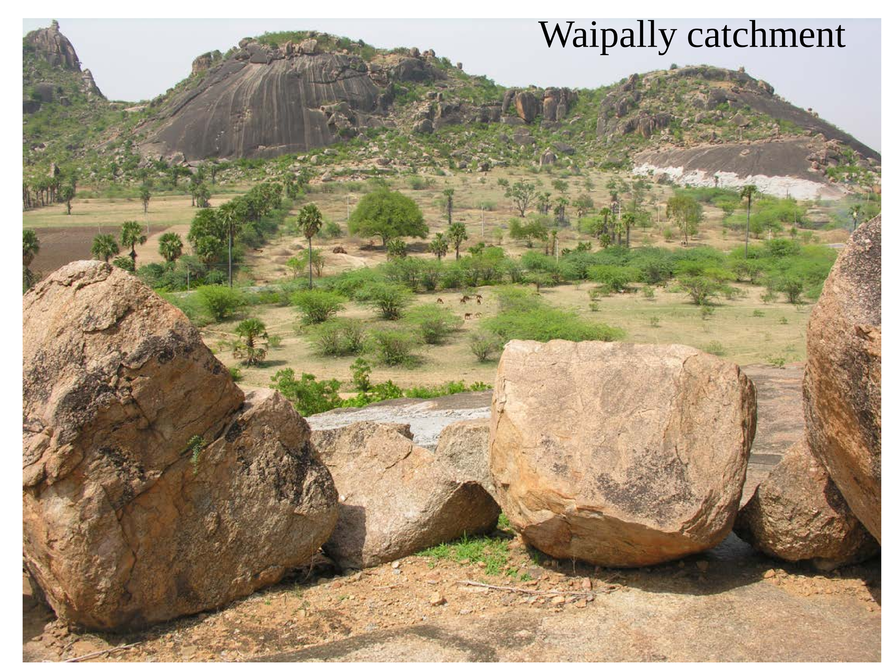
	Mineral contributions to weathering F removal, wt % 1A	2A	14A	16A	Average across sites	Mineral contributions to weathering F removal, fraction 1A	2A	14A	16A	Average across sites	Fraction of bedrock F
Fluorite	0.02736		0.01112		0.010	0.45		1.47		0.48	0.21
Apatite	0.01828	0.002294	-0.00325	0.010408	0.007	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	

Acknowledgements

For enabling access to field sites: Dr. S. Ahmed and Dr. S. Atal, National Geophysical Research Institute, India, and Dr. J. Perin, Indo-French Centre for Groundwater Research, India.
For laboratory assistance: Dr. Andrew Beard, Birkbeck College (electron microscopy), Dr. Ian Wood, UCL (XRD) and Mr. Tony Osborn, UCL (chemical analysis).
For Eng.Doc. Studentship funding (to BMH): EPSRC, NHM.

EPSRC Engineering and Physical Sciences Research Council

Maheshwaram catchment



An estimate of regolith age

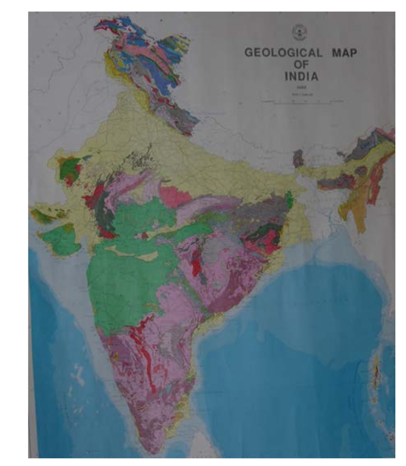
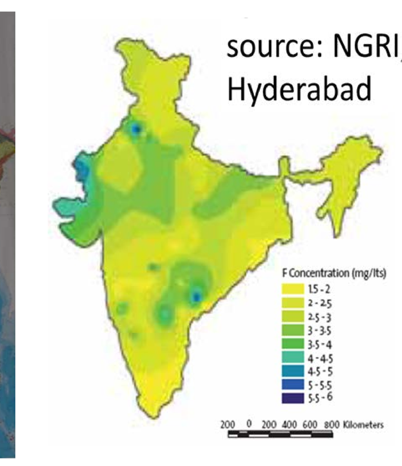
The cumulative weathering duration for the preserved regolith at Maheshwaram is estimated (below) at 250 - 380 Ka, close to the value of 223 Ka derived by Gunnell (1998) from denudation rates elsewhere in southern India. The method links the weathering flux of F and groundwater flux where bedrock/regolith pairs are coincident with measurements of groundwater [F-]. The method assumes (i) iso-volumetric weathering, (ii) groundwater [F-] is at equilibrium, and (iii) current climatic conditions are representative of average conditions over the duration of weathering so calculated.

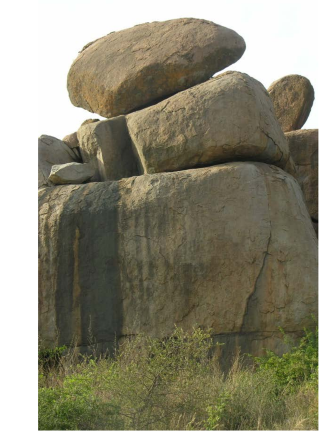
	M2	M3	M4
Bedrock F content, mg/kg	812	657	513
Regolith F content, mg/kg	84	15	9
F removed by weathering, mg/kg	728	642	504
Groundwater F content, mg/L	1.88	1.13	1.36
Groundwater volume for weathering, as effective depth (mm)	1.04E+07	1.53E+07	1.00E+07
Weathering duration	2.57E+05	3.78E+05	2.47E+05

[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; groundwater [F-] values from Atal (2008)].

Background

In India, fluorosis is the most widespread disease of geogenic origin (Chakraborti et al. 2011). The link between fluorosis and excessive F- in groundwater is well established (Nayak et al. 2009); more than 65 million people in India suffer from fluorosis related to F- in drinking water (Ayoob and Gupta 2006). In rural Andhra Pradesh, the most severely affected state, 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 *eg* at Maheshwaram (Sreedevi et al. 2006), in places up to 7 mg/l *eg* at Waipally (Reddy et al. 2010) and exceptionally as high as 20 mg/l (Rao et al. 1993). While groundwater host-rocks are acknowledged as the principal sources of regionally extensive F-, the contributions of specific F-bearing minerals and the relative significance of the bedrock and regolith as sources of F- to groundwater in the Archaen gneiss bedrock/regolith aquifer are disputed, as are explanations of seasonal and/or secular trends in groundwater [F-]. Safe management of the groundwater resource requires an improved understanding of the mineralogical sources of F, and their distribution.



The geological map (*left*, Geological Survey of India) shows the extent of the Peninsular Granite Complex. Excessive [F-] in groundwater is a widespread problem in Andhra Pradesh (National Geophysical Research Institute, Hyderabad), where regolith mantles an irregular surface of the fractured bedrock to a depth of about 10-20 m (*photographs, right*).

Questions and objectives

How is F distributed between its mineral hosts in Archaen gneiss bedrock and regolith? How effectively is F removed from its primary source(s) as the bedrock weathers? How is F mineralogical distribution related to present day groundwater [F-]?

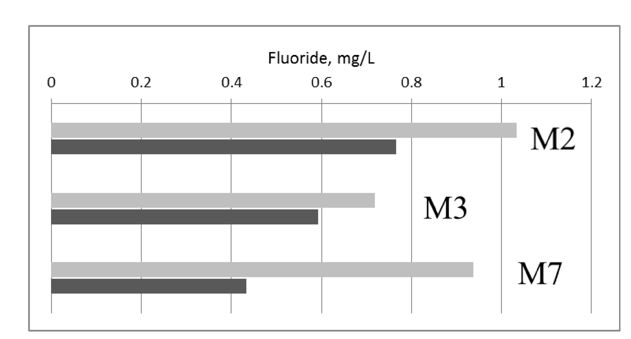
Addressing these questions, our primary objective is to quantify the present-day mineralogical sources of groundwater F- in Archaen bedrock/regolith environments, and the relative availability of F to groundwater from the bedrock and the regolith as discrete components of the aquifer. We use the results to investigate relationships with present-day groundwater [F-].

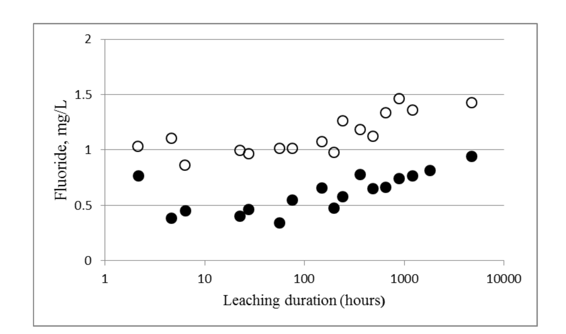
A secondary objective is to demonstrate the individual mineralogical contributions to the flux of F during past regolith development.

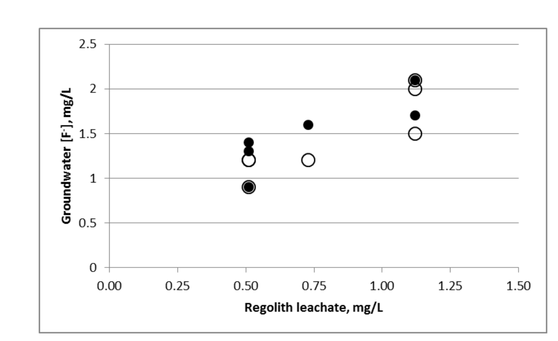
Thirdly, based on an inference of the cumulative groundwater flux and other simplifying assumptions, we make a first estimate of the regolith age.

Leaching experiments, field relations and significance of the regolith

Leaching experiments (*below left, and middle*) show that abundance of F is not a straightforward indicator of availability of F- to groundwater. The regolith is the dominant influence on groundwater [F-] and its seasonal variability, irrespective of the greater F content of bedrock and consistent with the suggestion (Sreedevi et al. 2006) that groundwater [F-] rises following groundwater recharge. Bedrock F content and groundwater [F-] are unrelated. A weak positive correlation is evident for the regolith under both pre-monsoon and post-monsoon conditions (Hallett et al. *under* review), and correlation of groundwater [F-] and leachate [F-] (*below right*) provides a positive test for the significance of the regolith. Results emphasise the dominance of the regolith as a source of groundwater F- in the Archaen bedrock/regolith aquifer of Andhra Pradesh. They suggest the contrasting timescales of F mobilisation from the regolith (seasonal) and the bedrock (1000s years, see *adjacent left* 'An estimate of regolith age'). Results also 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.







Left. Leachate [F-] from powdered regolith (light grey) and bedrock (dark grey) of the Peninsular Granite complex, Maheshwaram, at 2 hours leaching.
Middle. Evolution of leachate [F-] with time for Maheshwaram biotite granite and regolith, site M2.
Right . Groundwater [F-] v experimental leachate [F-] from regolith, Maheshwaram. Open circles: premonsoon; filled circles: post-monsoon

References

Atal, 2008 PhD Thesis, Osmania University (unpublished); Ayoob and Gupta 2006 Crit. Rev. Environ. Sci. Technol. 36, 433-487; Chakraborti et al. 2011 Environmental Science and Technology 45, 27-33; Dhakate et al. 2008 Journal of Environmental Management 88, 1373-1383; Gunnell, 1998 Geomorphology, 25, 135-153; Hallett, B.M. 2012 EngD Thesis, UCL (unpublished); Hallett et al., *under review* Journal of Hydrology Regional Studies; Kumar and Ahmed 2003 Current Science 84, 188-196; Nayak et al. 2009 Clin. Toxicol. 47, 292-295; Rao et al. 1993 Environmental Geology; Reddy et al. 2010 Chemical Geology 269, 278-289; Sreedevi et al. 2006 Environmental Geology 50, 1-11.