

Geochemistry and mineralogy of Triassic sandstones and implications for groundwater composition

D. A. SPEARS

Department of Geology, University of Sheffield, Sheffield S1 3JD

ABSTRACT. Borehole samples from the Wildmoor Sandstone Formation have been analysed for whole-rock major and trace elements and the mineralogy determined by X-ray diffraction and conventional thin sections. The forty-two samples studied were obtained from boreholes drilled in a long established effluent site and from control boreholes away from the site. Elements are associated with one or more of calcite, quartz, K-feldspar, and clay plus oxide. The most important mineralogical change due to current infiltration is progressive loss of calcite. Background element concentrations are established and only Pb, and in one sample Cu and Zn, are found in higher concentrations representing anthropogenic additions to the system.

THE geochemistry of sandstones is a function of the mineralogy, and this reflects the erosional, depositional, and diagenetic processes. A decrease in grain size, or in the quality of sorting, produces an increase in the proportion of clay minerals relative to the resistate minerals. Element concentrations would be expected to rise because the main resistate mineral, quartz, acts as a diluent for most elements. If the sandstones are immature then the feldspar/quartz ratio is higher and again both major and trace element concentrations will be higher. Diagenetic changes are also important, especially as sandstones may behave as open systems for long periods of time. It has been established for many years that heavy minerals may be modified by intrastratal solutions. More recently the role that porewaters play in the development of secondary porosity has been appreciated. Sandstones may also be either a source or a repository for mineralizing solutions. Sandstones comparable in facies to those studied in this work are thought to be the source of the Upper Permian 'Kupferschiefer' mineralization. Arising from this possibility the geochemistry and mineralogy of sandstones was studied by Rentzsch and Kampe (1979). Detailed analyses of red bed sediments from SW England were made by Cosgrove (1973) with an important aim of providing more information

on oxidized sediments as opposed to reduced sediments, mainly black shales. Post-depositional changes are also thought to be important in the formation of the red colouration of these beds (see Glennie, 1972).

The present study was initiated because of an interest in the reactions between pore fluids and the constituents of sandstones, but in a very specific situation. The Triassic sandstones of interest are those which underlie an effluent spreading site at Whittington Hall (NGR SO 859 826). Primary sewage effluent has been spread on this site for close to 100 years. The underlying aquifer is pumped for public supply and pollution of the groundwater is clearly a possibility. An investigation of this site was conducted by the Water Research Centre in conjunction with the Severn-Trent Water Authority. Porewaters and groundwaters were extracted from boreholes and analysed. Compositional changes along the infiltration pathway and particularly with depth in the unsaturated zone were detected. In parallel with this work the whole-rock geochemistry and mineralogy were studied in the University of Sheffield, to provide supplementary information, and in particular to detect either loss or gain of elements from the system. In order to achieve this the natural background variation of elements and their locations in the rock had to be established before the anthropogenic input was considered.

Geology. The effluent spreading site is centred on Whittington Hall which is approximately 4 km SW of Stourbridge. Extending to a depth of between 80 and 95 m below the site are red sandstones belonging to the Wildmoor Sandstone Formation (formerly 'Bunter Upper Mottled Sandstone', Warrington *et al.*, 1980), which overlies the beds belonging to the Kidderminster Formation (formerly 'Bunter Pebble Beds'). In the Kidderminster Formation rudaceous deposits of two types occur, one of local origin interpreted as gravel fans at the mouth of wadis emerging on to the

depositional plain from a mountainous area and the other, with well-rounded pebbles of more distant origin, probably transported by a major river system from the south. Rounded extraclasts become less frequent higher in the sequence and their ultimate disappearance marks the ill-defined base of the Wildmoor Sandstone Formation (Warrington *et al.*, 1980). The overall decrease in grain size with time records a progressive diminution of the amount and velocity of flooding and is accompanied by a reduction in topographic relief from uplands to plain (Wills, 1976). The sediments were deposited by water as indicated above, in an environment described as continental fluvial (Warrington *et al.*, 1980) in which alluvial fans pass laterally into an alluvial plain. The red colouration of the sandstones suggested to Wills (1976) lateritic weathering in the source area with ferric oxides colouring the sediment except where plant material was sufficiently abundant to produce a reducing environment. There is, however, the possibility that the red colouration is diagenetic as described by Glennie (1972). Furthermore if laterites were common then this should be reflected in the clay mineralogy with kaolinite abundant, but in the mudrocks studied by Jeans (1978), mainly from the overlying Mercia Mudstone Group, the clay minerals comprise mica and minor chlorite, thought to be detrital in origin, together with an assemblage of neoformed Mg-rich clay minerals.

Analytical methods. Borehole samples for whole-rock chemical analysis were crushed in a Tema disc mill and further ground by hand in an agate mortar. Na was determined by atomic absorption and the remaining major elements by X-ray fluorescence (XRF) spectrometry using the fusion method of Norrish and Hutton (1969). The trace elements Zn, Cu, Ni, Pb, V, Mn, Cr, Zr, Y, Sr, and Rb were also determined by XRF using pressed powders. All the crushed samples were examined by X-ray diffraction using back-filled powder mounts and a smaller number of clay fractions separated from uncrushed samples were investigated using smear mounts. Standard thin sections were prepared from resin impregnated material. Porewaters and groundwaters were also extracted from the borehole material by means of centrifuge extraction and analysed by atomic absorption, but full details of these analyses are not included in this paper.

Sample location. The sandstone samples were obtained from four of the boreholes drilled by the Water Research Centre. Two of the boreholes drilled in 1977 were sampled at 2 m intervals from 1 to 29 m. One borehole was sited in an area where contamination was anticipated (WL borehole NRS SO 866 826) and the other was located to the south

of the effluent site (BTF Borehole, NGR 863 807). Samples were obtained from a third borehole in 1978 (WRH borehole, NRS 866 824) and six samples were analysed covering a depth range 1–26 m. The saturated zone was sampled in a deeper borehole (BTL borehole, NGR 865 805) off the effluent spreading area but down the groundwater gradient. Six samples from this borehole were analysed from a depth of 31 m to 86 m. The base of the Wildmoor Formation was recognized by the Water Research Centre in deep boreholes by an increase in grain size and formation resistivity and a decrease in the radioactivity on the gamma ray log. By reference to adjacent deep boreholes the WL samples are thought to be from 115 to 85 m above the base of the Wildmoor Formation, the WRH samples from 105 to 75 m, the BTF samples from 80 to 50 m, and the BTL samples from 55 to 5 m.

Petrography. The grain size of the sandstones, which are all red in colour, ranges from medium to very fine grained. In the two boreholes with the greatest density of sampling the median grain decreases with depth in one (WL borehole) from 2.3ϕ to 3.2ϕ and increases in the other (BTF borehole) from 2.8ϕ to 1.5ϕ . Cycles in these sandstones were noted by Wills (1976). Depth-related changes in the geochemistry were therefore detected in the present work, but because the grain size trends are in opposite directions superimposed changes due to modern infiltration may be identified.

In thin section quartz is seen to be dominant, but feldspars are also important. Point counting of stained grains gave the average values of 79% quartz, 19% K feldspar and 2% albite. Comparable values were obtained by: (a) recasting chemical analyses of size fractions (Table I), assuming feldspars are absent in the clay fraction, which gave 17.6% K feldspar and 1.6% albite; and (b) selective dissolution of coarse fractions which gave 15.0% K feldspar and 1.2% albite. The feldspar content indicates a sub-arkose classification for the sandstones. A depth-related variation in the abundance of feldspars was not detected, indicating lack of appreciable reaction with porewaters even in areas of enhanced infiltration. In the overlying Bromsgrove Sandstone Formation up to 25% feldspar was recorded by Ali and Turner (1982). These authors noted the ubiquitous occurrence of authigenic K feldspar, virtually pure $KAlSi_3O_8$, on cores of detrital feldspar and a diagenetic sequence consisting of: (1) illite; (2) quartz; (3) K-feldspar; (4) illite; and (5) kaolinite. In the present work authigenic K-feldspar overgrowths were observed but the percentage would appear to be small.

Calcite was the only carbonate detected and its

TABLE I. Mean analyses and standard deviations of forty-two red sandstones, Whittington

	Means and standard deviations	Red sandstones (Cosgrove, 1973)	Clay fraction	
			< 2 μm	> 150 μm
SiO ₂	83.62±4.52%	—	49.63	89.94
TiO ₂	0.26±0.09%	—	0.44	0.09
Al ₂ O ₃	5.94±1.55%	7.2	20.94	4.83
Fe ₂ O ₃	1.58±0.60%	1.6	} 8.24	} 0.66
FeO	0.21±0.10%	—		
MgO	0.60±0.30%	0.3	2.42	0.22
CaO	1.56±2.18%	0.15	1.50	0.11
K ₂ O	2.91±0.65%	3.2	3.38	3.28
Na ₂ O	0.20±0.06%	0.5	0.09	0.20
P ₂ O ₅	0.10±0.04%	0.05	0.19	0.06
Ni	7± 3 ppm	8		
Mn	460±390 ppm	282		
V	22± 6 ppm	20		
Cr	33± 11 ppm	—		
Zn	28± 14 ppm	6		
Cu	8± 3 ppm	9		
Rb	81± 17 ppm	72		
Sr	58± 12 ppm	47		
Y	16± 7 ppm	13		
Zr	185± 93 ppm	107		
Pb	33± 18 ppm	13		
Ba	385± 61 ppm	375		

concentration is depth related. Away from the irrigated area calcite appears at a depth of 7 m (BTF borehole). In the irrigated area calcite was not detected in the shallow boreholes, that is down to 29 m (WL and BTL boreholes) but calcite was detected by means of X-ray diffraction at depths of ≥ 46 m in samples from an additional deep borehole in the irrigated area. Based on the chemical analyses the calcite concentration at depth is fairly uniform with an average value of $4.5 \pm 1.8\%$ ($n = 15$) but with the occasional sample much higher (14.7 and 16.2%). Carbonate is present both as grains and as cement, and it is the latter which is responsible for the higher concentrations recorded in some samples.

In the whole-rock X-ray diffractograms small clay peaks are visible. Clay fractions (< 2 μm) were separated from a number of samples for a more detailed investigation. The clay minerals are of interest in studies of porewater reactions in sandstones because of their reactive nature, which is both a function of size and structure. The quartz grains, on the other hand, although they are the major component are less reactive. Clay fractions were separated from the following samples: BTF borehole 1 m, 15 m, and 29 m, WL borehole 1 m, 15 m, and 29 m, and WRH borehole 1 m, 5 m, 10 m, 15 m, 20 m, and 26 m. Samples were prepared

as smear mounts, and run air dried, glycolated, heated at 350° and 550 °C. A representative diffractogram is shown in fig. 1. The smectite has a basal spacing of 15.0 Å air dried, 17.0 Å glycolated, and 10 Å when heated. Mica is present in all the samples based on the 10 Å peak which is unaffected by glycolation and heat treatment. Chlorite is also present. The 001 reflection appears on the air-dried mount as either an inflection on the smectite peak or as a distinct peak depending on the relative proportions of the two minerals. The 001 peak is more clearly seen on the glycolated and heat treated runs, although some variation was noted in the heat stability. There is a major peak corresponding to the 002 chlorite which suggests that kaolinite is present, unless of course the chlorite is Fe rich in which the 'even' reflections are strong. Heating at 550 °C (fig. 1) greatly reduces the 7 Å peak intensity, with little change to the 14 Å peak demonstrating the presence of kaolinite. The behaviour of the chlorite does vary however, and in some of the samples heating at 550 °C, following the 350 °C heating, eliminates the chlorite peaks. Although it is not possible to resolve the 002 chlorite and the 001 kaolinite peaks this is not the case for the 004 chlorite and 002 kaolinite peaks on the air-dried traces. Most of the diffractograms are similar to the traces shown on fig. 1, but there are some

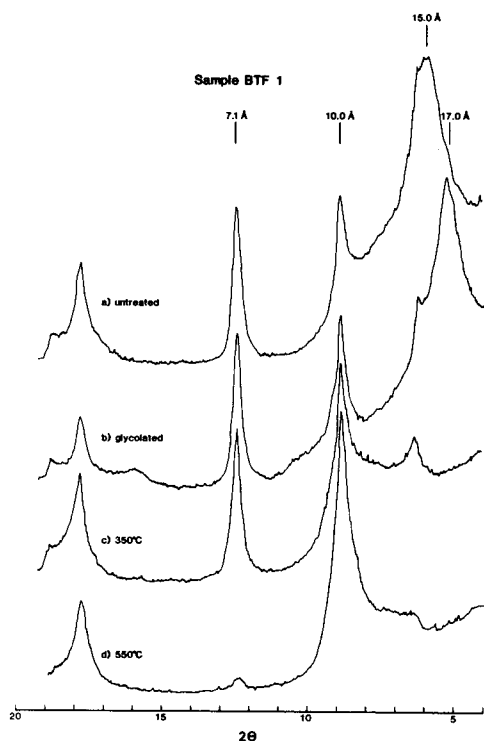


FIG. 1. X-ray diffractogram of clay fraction ($< 2 \mu\text{m}$) from sample BTF 1 m. Sample prepared as smear mount and run air-dried, glycolated, heat treated at 350°C for 1 hour and at 550°C for 1 hour. Cu-K α radiation.

systematic differences. Thus in the WL and WRH samples the 7 \AA peak intensity is reduced by 50% relative to the 10 \AA peak. At a depth of 29 m in the WL borehole the proportion of smectite is comparable with the samples from the other boreholes, but at shallower depths progressively less smectite is present. In the BTF samples the chlorite does survive the 550°C heat treatment, although there is evidence for mixed-layer clay with chlorite layers at about 12 \AA (fig. 1). In the other samples, which are all from the irrigation site, the chlorite is not stable with heating and a discrete 14 \AA peak is absent, but again there is mixed layer clay at about 12 \AA .

Discussion of the mineralogy. The feldspathic nature of the sandstones is consistent with erosion in a semi-arid climate with little chemical weathering. Furthermore, primary feldspar-bearing rocks must have been exposed in the sediment's source area in addition to sedimentary rocks. The occurrence of large, unweathered feldspar in the overlying formation led Wills (1976) to the same

conclusion. The plagioclase feldspar content was probably higher, unless the source rocks were somewhat unusual, and there may have been loss due to intrastratal solutions. In the context of groundwater quality and infiltration reactions a depth variation in feldspar abundance was not detected, indicating lack of appreciable reaction with porewaters. Similar observations were made for infiltration through glacial sediments (Spears and Reeves, 1975) and in Triassic sandstones to the north of the present area (Edmunds and Morgan-Jones, 1976).

Calcite is absent in near-surface sediments to a depth of 7 m under conditions of natural infiltration and to a depth of 46 m under enhanced infiltration. This variation is consistent with calcite reaction with the infiltrating porewaters and progressive removal from the surface downwards. The attainment of equilibrium is known to take place quickly (Jacobson and Langmuir, 1974) and this is consistent with the distribution of calcite in the samples because there is not a progressive increase in the amount of calcite with depth. The infiltrating porewaters reach the calcite-bearing sediment where they react and then pass on downwards with no further reaction. Saturation of the porewaters with respect to calcite would therefore be predicted for the groundwater in the aquifer in this area. Under-saturation was noted in groundwaters to the north by Edmunds and Morgan-Jones (1976) which they attributed to a deficiency of carbonate in the sandstones. There is thus an indication that lateral differences do exist.

The variation in clay mineralogy, which may be due to increased infiltration, is evident in the alteration of the chlorite based on its lack of structural stability on heating. In the irrigation area the smectite abundance is low near-surface in one borehole but not in another and the variation is therefore presumably original.

The clay fractions separated from the sandstones in the present work have features in common with the assemblages recorded in the literature (Henson, 1973; Jeans, 1978) but apart from smectite, Mg-rich clays indicative of hypersaline conditions are absent. The mica and chlorite is probably detrital and could well be recycled from Palaeozoic and older rocks. Some of the kaolinite could also be recycled, but in this case from upper Palaeozoic rocks. Mudrock intraclasts are common in the sandstones and this is certainly one means by which detrital clays could be introduced into a moderately well sorted sandstone. Undoubtedly some kaolinite is associated with the feldspars but in what proportion and when it developed are unknown. Smectite may have formed in the soils on the neighbouring uplands, and certainly the weathering of micas is

one well-established pathway for its formation. Volcanic pebbles are recorded from the sandstones (Wills, 1976) and smectites could be associated, possibly either pre- or post-sedimentation age. SEM work by Ali and Turner (1982) on the overlying sandstones has revealed diagenetic illite and kaolinite, and therefore in the present samples the presence of some diagenetic illite and kaolinite would be anticipated.

Discussion of the geochemistry. The mean composition of the sandstones is given in Table I. The importance of quartz is seen in the high SiO₂ concentration. In correlation analysis the correlations involving SiO₂ are all negative, indicating the diluting effect of quartz on all other components of the sediment and illustrating the problems of closure correlation (Chayes, 1971). Correlations of a number of elements with Al₂O₃, K₂O, Fe₂O₃, FeO, and MgO are shown in Table II. The only positive significant correlation involving CaO is with Mn and is due to variations in the calcite abundance. K-feldspar constitutes an important component of the sediment and a positive correlation with quartz might be anticipated, but in fact feldspar and clay are antipathetic in abundance to quartz. This suggests that the quartz and feldspar grain size distributions are not identical and the feldspar is concentrated in the fine sand fractions in an analogous manner to the sandstones described by Odom (1975). Al₂O₃ is present in both feldspars and clay minerals and the correlations

involving Al₂O₃ (Table II) reflect the variable influence of these two fractions. Thus K₂O is present in K-feldspar and the clay fraction (illite), whereas MgO is only associated with the clay fraction and in consequence the value of the correlation coefficient with Al₂O₃ is reduced compared with K₂O.

Fig. 2 shows the plot of K₂O vs. Al₂O₃. The positive intercept on the K₂O axis shows that as the Al₂O₃ concentration increases so the K₂O/Al₂O₃ ratio decreases, which is due to the increased clay contribution associated with a decrease in the mean grain size of the sediment. At the minimum recorded Al₂O₃ concentration the clay content is calculated to be 8% and the K-feldspar 9% (based on the analysis of the < 2 μm clay fraction, Table I) and for the mean Al₂O₃ and K₂O concentrations the respective values are 16% clay and 14% feldspar. Both increase as the grain size decreases, but the clay increase is proportionally greater. These calculations also demonstrate that the major control on the K₂O concentration is K-feldspar rather than illite.

Rb, Sr, and Ba correlate well with K₂O and with each other, and are compatible with known concentrations in K-feldspar. The regression equations of these elements with Al₂O₃ (Table III) are also similar to K₂O in that they all have a positive intercept on the y axis.

The correlation between MgO and Al₂O₃ (Table II) is due to clay variation as noted above. Similar in behaviour to MgO is Fe₂O₃, which is interpreted to mean that the iron oxide is clay associated probably because of surface area. The elements K₂O, Rb, Sr, and Ba do not correlate with either

TABLE II. Product moment correlation coefficients (Values less than 95% confidence level for independent variables not given)

	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	FeO	MgO
Al ₂ O ₃	—	—	—	—	—
K ₂ O	0.93	—	—	—	—
Fe ₂ O ₃	0.40	—	—	—	—
FeO	0.50	0.36	0.37	—	—
MgO	0.40	—	0.82	0.44	—
CaO	—	—	—	—	—
P ₂ O ₅	0.82	0.72	0.63	0.47	0.64
Ni	0.73	0.59	0.54	0.44	0.48
Mn	—	—	0.52	—	0.51
V	0.62	0.41	0.78	0.56	0.64
Cr	0.68	0.55	—	0.57	—
Zn	—	—	—	0.32	—
Cu	—	—	—	—	—
Rb	0.79	0.86	—	0.34	—
Sr	0.85	0.87	—	0.39	—
Y	0.64	0.56	0.71	0.42	0.68
Zr	0.65	0.55	—	—	—
Pb	0.67	0.67	0.43	—	0.45
Ba	0.75	0.82	—	—	—

TABLE III. Reduced major axis regression equations, elements vs. Al₂O₃ red sandstones, Whittington

Regression equations	95% confidence limit on intercept
K ₂ O = 0.42 Al ₂ O ₃ + 0.42	± 0.29
Rb = 10.8 Al ₂ O ₃ + 16.6	± 13.0
Sr = 7.6 Al ₂ O ₃ + 12.5	± 7.4
Ba = 39.3 Al ₂ O ₃ + 151	± 50.0
Fe ₂ O ₃ = 0.39 Al ₂ O ₃ - 0.73	± 0.68
FeO = 0.06 Al ₂ O ₃ - 0.17	± 0.10
MgO = 0.19 Al ₂ O ₃ - 0.54	± 0.34
P ₂ O ₅ = 0.26 Al ₂ O ₃ - 0.06	± 0.03
Pb = 11.7 Al ₂ O ₃ - 36.3	± 16.5
Ni = 2.23 Al ₂ O ₃ - 5.95	± 2.94
V = 4.08 Al ₂ O ₃ - 2.10	± 6.07
Cr = 7.05 Al ₂ O ₃ - 8.80	± 9.88
Y = 4.73 Al ₂ O ₃ - 9.60	± 6.40
Zr = 59.5 Al ₂ O ₃ - 158	± 86

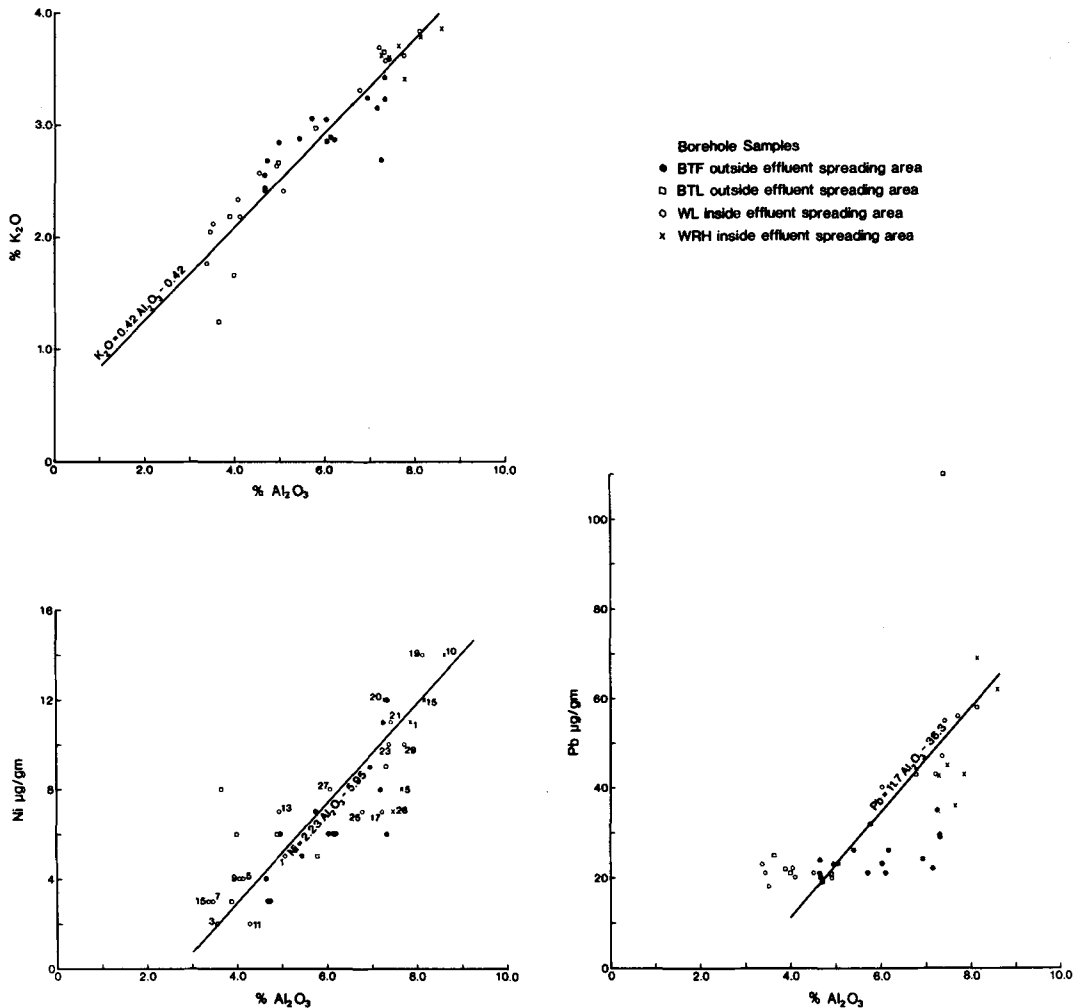


FIG. 2. Plots of K₂O, Ni, and Pb concentrations against Al₂O₃ concentrations in borehole samples. The samples from the four boreholes are indicated. Two of the boreholes are inside the effluent spreading area (WL and WRH) and two outside (BTF and BTL). Reduced major axis regression equations are shown.

MgO or Fe₂O₃ which provides additional evidence of the feldspar control. P₂O₅, Ni, V, Y, and Pb (Table II) correlate with Al₂O₃, K₂O at a lower significance level, and also with MgO and Fe₂O₃, unlike Rb, Sr, and Ba. These elements are clay or oxide associated, and this is also seen in the regression equations with Al₂O₃ where there is a negative intercept on the y axis (Table III), unlike the feldspar related elements.

The absence of correlations, as for example with Zn and Cu, could mean that these elements are either associated with more than one fraction of the sediment which are antipathetic in their distribution, or alternatively that the original distribu-

tions are overshadowed by changes resulting from weathering and effluent infiltration. The mean Zn concentration is $25.1 \pm 8.6 \mu\text{g/gm}$ ($n = 30$), but in one sample a value of $96 \mu\text{g/gm}$ was recorded which lies outside the normal distribution. In the same sample the Cu concentration is $20 \mu\text{g/gm}$ compared with a mean value and standard deviation of $8.1 \pm 2.1 \mu\text{g/gm}$ ($n = 30$), which is also significantly different to the normal distribution. This sample is from the top of a contaminated borehole and the high concentrations are therefore attributed to effluent infiltration. Exclusion of this sample from the correlation matrix on the grounds of non-normal Cu and Zn distributions failed to

reveal any specific associations in the remaining samples.

The cases considered above represent two extreme positions, on the one hand the external input swamps the natural variation and on the other the element distributions are considered in terms of mineral abundances without reference to depth in the profile and to possible anthropogenic gain or loss from the system. There is, of course, the possibility of intermediate situations where there is a natural predictable background concentration with a detectable external addition. This possibility is explored in the case of Ni on fig. 2. Sample depths in the boreholes in the effluent-spreading site are shown. The samples which are potentially polluted neither differ as a group from the control samples nor show a systematic depth-related divergence from the general trend. In the case of Ni, contamination of only a few $\mu\text{g/gm}$ would have been detected from the whole-rock data. Similar analysis of the other elements correlating positively with Al_2O_3 (Table II) also failed to detect whole-rock contamination with one possible exception. This exception is Pb which is plotted against Al_2O_3 on fig. 2. At low Al_2O_3 concentrations the Pb values are very similar for samples from unpolluted and polluted boreholes. At higher Al_2O_3 concentrations (increase in clay fraction) the Pb concentrations are higher in all the samples from the polluted boreholes, including two samples from the saturated zone down the groundwater gradient (BTL samples), and it must be concluded that the whole-rock samples are contaminated. It is noteworthy that the contamination is related to the abundance of the clay fraction irrespective of borehole depth in the irrigated area. The nature of the association with the clay fraction has not been established but exchange reactions, mainly smectite, could be involved or possibly fixation in degraded micas.

The mean Fe_2O_3 concentration in the sandstone is 1.58% and the FeO 0.21% (Table I). The FeO is similar in behaviour to MgO and hence is thought to be clay associated. The movement of porewaters through the sandstones from the present ground surface has not influenced the Fe_2O_3 -FeO distributions. Although the effluent is organic rich, reduction of Fe_2O_3 has not occurred in the borehole samples and hence in most of the unsaturated zone. Significant reduction of iron would have destroyed the MgO- Fe_2O_3 correlation. This is also borne out by the FeO/ Fe_2O_3 ratio which is marginally higher if the sandstone is clay rich irrespective of depth below surface. This is consistent with the measurement of positive Eh values, and the presence of dissolved O_2 in groundwaters in the Triassic sandstones to the north of the present area (Edmunds and Morgan-Jones, 1976).

The survival of FeO on the other hand does require location in inaccessible structural sites. In spite of the red colouration of the sandstones the concentration of iron is not particularly high. The concentration does increase as the grain size decreases and a separated clay fraction has a higher iron content (8.2% Fe_2O_3). This information on the distribution of iron, coupled with the evidence of lack of mobility supports the concept of an initial association of iron with the fine fraction, that is at the time of sedimentation, rather than the diagenetic destruction of ferromagnesian minerals during diagenesis.

Average concentrations for the red sandstones analysed by Cosgrove (1973) are presented in Table I. The concentrations of most elements are very similar indeed to those recorded in the present work, indicating comparable mineralogical controls. The Pb and Zn concentration is however, higher in the present samples thus supporting the concept of anthropogenic addition. The mean Pb concentration in the present samples is in fact greater than values quoted by Rentzsch and Kampe (1979) for late Variscan red sandstones in Central Europe which are considered to be Pb-specialized.

Conclusions. Red sandstones from the basal 100 m of the Wildmoor Sandstone Formation were sampled from boreholes in an effluent spreading site and from control boreholes outside. The main conclusions reached are as follows.

(a) The grain size variation of the sandstones, from medium to fine grained, is an important control on the mineralogy, in particular the feldspar-clay proportions, and thus on the geochemistry.

(b) Identification of the mineralogical control on trace metal concentrations enables the natural background variation to be closely defined and small anthropogenic additions to be detected. Anthropogenic Pb is present in samples with a high clay content within the effluent spreading area and also outside in the saturated zone down the groundwater gradient. Addition of Cu and Zn was also detected in one near-surface sample.

(c) The high K-feldspar content (19%) of the sandstones is consistent with weathering in a semi-arid environment and so too is the clay mineral suite. The contribution of Palaeozoic rocks to the latter is thought to be important. Evidence of clay formation in hyper-saline conditions is lacking.

(d) Mineralogical changes due to weathering are alteration of chlorite and dissolution of calcite to depths directly related to the volume of infiltration. Saturation of groundwaters with respect to calcite is indicated.

(e) Although considerable amounts of organic

matter have been added to the system in the irrigation area there is no evidence of iron reduction and mobility, which indicates that the porewaters are at a positive Eh as they are in the aquifer elsewhere.

Acknowledgements. The work was undertaken in conjunction with the Water Research Centre and the Severn-Trent Water Authority, and I would particularly like to thank Dr L. Clarke, Dr K. Whitelaw, Mr K. Edworthy, and Dr A. Skinner. Responsibility for the views expressed in this paper lies, however, with the author.

REFERENCES

- Ali, A. D., and Turner, P. (1982) *J. Sed. Petrol.* **52**, 187-97.
- Chayes, F. (1971) *Ratio Correlation*. University of Chicago Press, 99 pp.
- Cosgrove, M. E. (1973) *Chem. Geol.* **11**, 31-47.
- Edmunds, W. M., and Morgan-Jones, M. (1976) *Q. J. Eng. Geol.* **9**, 73-101.
- Glennie, K. W. (1972) *Bull. Am. Assoc. Petrol. Geol.* **56**, 1048-71.
- Henson, M. R. (1973) *Proc. Geol. Assoc.* **84**, 429-45.
- Jacobson, R. L., and Langmuir, D. (1974) *Geochim. Cosmochim. Acta*, **38**, 301-18.
- Jears, C. V. (1978) *Phil. Trans. R. Soc. A*, **289**, 549-639.
- Norrish, K., and Hutton, J. T. (1969) *Geochem. Cosmochim. Acta*, **33**, 431-453.
- Odom, I. E. (1975) *J. Sed. Petrol.* **45**, 636-50.
- Rentzsch, J., and Kampe, A. (1979) In *Origin and distribution of the elements* (Ahrens, L. A., ed.). Second Symposium, Paris 1977, Pergamon, 751-66.
- Spears, D. A., and Reeves, M. J. (1975) *Geol. Mag.* **112**, 585-91.
- Warrington, G., Audley-Charles, M. G., Elliott, R. E., Evans, W. B., Ivimey-Cook, H. C., Kent, P. E., Robinson, P., Shotton, F. W., and Taylor, F. M. (1980) *A correlation of Triassic rocks in the British Isles*. Geol. Soc. London, Special Report No. 13, 78 pp.
- Wills, L. J. (1976) *Rep. Inst. Geol. Sci.* No. 7612, 211 pp.

[Revised manuscript received 4 November 1982]