SANDROCK SPRING AND SHANKLIN SPA: CONTRASTING CHALYBEATE WATERS FROM THE LOWER GREENSAND OF THE ISLE OF WIGHT

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Chalybeate mineral springs in the Isle of Wight Lower Greensand were first recognised in the 17th Century although no development took place. From 1808 the virtues of Sandrock Spring at Niton were touted by a local physician, Thomas Laurence Waterworth. Chemical tests showed that it had high concentrations of both iron and aluminium. By 1896 another spring had been transformed into the grandly named Shanklin Royal Chalybeate Spa. Although patronised for a few years neither development prospered and little evidence of their existence remains today. The Sandrock Spring was derived from quartz sands of the Sandrock Formation whereas Shanklin Spa obtained its water from glauconitic sands lower in the succession within the Ferruginous Sands Formation. Iron concentrations of over 1000 mg/l were measured at Sandrock compared with 20-30 mg/l at Shanklin. The contrasting composition of the two springs results from the differing mineralogy of their host rocks; the presence or absence of carbonate controlling the concentration of iron in solution. The strongly acidic "vitriolated chalybeate" waters, such as that found at Sandrock, did not lose their iron as rapidly as the weakly acidic "carbonated chalybeates" found at Shanklin and were highly prized by spa physicians.

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INTRODUCTION

On the Isle of Wight, the presence of springs impregnated with minerals was recognised by early topographers (Worsley, 1781) and both sulphur and chalybeate springs were recorded in the parish of Chale, close to the southernmost point of the island (Figure 1). At this time the springs were not developed although tests had shown that a chalybeate spring at Blackgang Chine was stronger than the water of Tunbridge Wells. This situation was to change in the early years of the 19th Century when a local surgeon from Newport, Thomas Laurence Waterworth, set out to locate and investigate the springs. It is likely that his quest was prompted, at least in part, by the war in Europe which since 1793 had closed continental spas to English visitors. After the initial shock, domestic spa life was boosted so that the social lives of the better-off could carry on much as before. This resulted in the promotion of new English spas, at least thirteen of which were founded between 1800 and 1809 (Hembry, 1990). Amongst these was a spring discovered by Waterworth, which he named the Sand Rock Spring after the bed of loose quartzose sand from which it issued. Chemical analysis demonstrated that it had a unique composition and for some years it was marketed as a powerful tonic.

Worsley (1781) also noted a spring, impregnated with alum, which had been discovered at Shanklin (Figure 1) by Dr Fraser, physician to King Charles II. For some time this had been drunk with success, but had become *"gradually disused, and at length neglected"* (Worsley, 1781, p. 6). Alexander Fraizer (Fraiser or Fraser) received a warrant for the position of principal physician to the King in 1664 (Dingwall, 2004). Charles II subsequently visited the Isle of Wight on a number of occasions (Albin, 1795) during any of which his physician

could have sampled water from the spring. However, any fame which the spring enjoyed probably died with the Stuart monarchs and it was to be 200 years before it was to be reborn as the Royal Shanklin Spa.

In this paper the history and hydrogeology of these two contrasting mineral springs on the Isle of Wight is examined. Although both arise from the Cretaceous Lower Greensand Group, and are chalybeate waters, they are geochemically distinct and illustrate the dominant control of rock mineralogy on groundwater composition.

SANDROCK SPRING

The discovery of the Sand Rock (later Sandrock) Spring was announced by Waterworth in a letter published in the November 1811 issue of the Monthly Magazine (Waterworth, 1811). This was preceded by a chemical account of the spring published in the first volume of the Transactions of the Geological Society of London (Marcet, 1811), which appeared in the latter half of 1811. Of the 18 papers included, it stood out as the only paper not devoted to either mineralogy or to regional geological studies (Davies, 2007). A more detailed account of the discovery, including a letter from Waterworth dated October 1st 1811, together with details of the medical effects of the water and directions for its consumption, are contained in an undated pamphlet by a local army physician, William Lemprière (Lemprière, 1812). A date of 1812 has been assumed for this pamphlet, as it includes correspondence dated as late as November 4th 1811. However, the British Library catalogue assigns an 1811 date. A second edition, also undated,

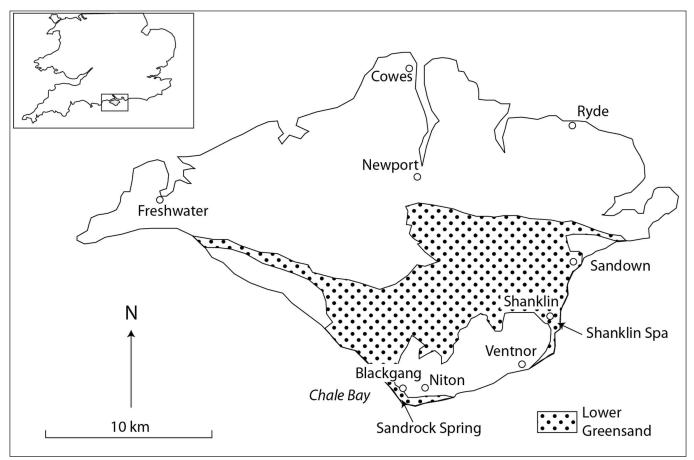


Figure 1. Map of the Isle of Wight showing the outcrop of the Lower Greensand Formation and the localities mentioned in the text.

omits the frontispiece and the decorative title page but adds a list of errata. This edition was reviewed by the *Gentleman's Magazine* in its March 1815 issue and it is possible that it was not published until 1814 (Lemprière, 1814).

Probably in 1807, Waterworth first explored the area around Chale Bay looking for the chalybeate spring at Blackgang Chine described by Worsley (1781). His visit was unsuccessful, but he returned and tasted every streamlet he could find that flowed down the cliff, eventually locating three springs of interest, including that at Blackgang. On a further visit he collected water from each of the springs. On the advice of William Saunders, a Fellow of the Royal Society and from 1808 a member of the Geological Society, at that time on a visit to the island, he elected to concentrate further work on a small stream, containing yellow particles of sulphur, which he described as an aluminous chalybeate with an astonishing taste (Lemprière, 1812). Saunders had been a physician at Guy's Hospital until his retirement in 1802 (Moore, 2004) and was the author of a treatise on mineral waters (Saunders, 1800).

Heavy rainfall in the latter part of 1808 precluded further progress until the following spring when Waterworth was able to follow the stream back to its source. Here he scooped out a hollow in the sand rock which rapidly filled with water. This was undiluted by mixing with other streams and hence more highly mineralised than the water he had first found on the beach. He immediately obtained a lease to the exclusive rights to the soil from the local lord of the manor. Over the next few months he excavated into the sand rock and formed an arched enclosure around the spring using stone procured on site. Water oozed from the surrounding strata into a reservoir at the rate of three to four hogsheads in 24 hours (862-1150 l/day) (Lemprière, 1812). Unfortunately there was no regular road to the spring which was in a landslipped area, backed by high cliffs. Known as the Undercliff, it was covered by broken rock with little vegetation. Waterworth accessed the spring from Niton (Figure 1), taking a cart to the edge of the landslip and

then carrying water from the spring using two small tubs suspended one on each side of his horse which he emptied into a larger tub in the cart. He recognised that, provided precautions were taken to exclude air, the water could be transported without the iron coming out of solution.

Saunders asked another Guy's physician, Alexander John Gaspard Marcet, to examine the water. Marcet had been elected to Fellowship of the Royal Society and Membership of the Geological Society in 1808. In 1805 he had analysed a chalybeate spring at Brighton (Marcet, 1805) and was to become a skilled analytical chemist analysing sea water and animal fluids as well as mineral waters (Coley, 2004). Marcet's account of the Sandrock water (Marcet, 1811) includes a description of the site by his friend Jean-François Berger who had explored the geology of the Isle of Wight with the financial support of a number of subscribers, many of whom were members of the Geological Society (Davies, 2007). According to Berger, the spring was 130 ft (40 m) above sea level and about 150 yards (137 m) from the shore.

Waterworth began to prescribe the mineral water in his practice in Newport finding it useful in a range of complaints and at the end of 1809 asked William Lemprière to undertake a trial of the water at the Army Depot Hospital, at Albany on the Isle of Wight. Born in Jersey, Lemprière was a respected military physician who amongst other postings had spent five years in Jamaica, subsequently writing an account of the diseases he encountered there (Lemprière, 1799). The Depot Hospital received invalids from abroad, particularly soldiers debilitated or otherwise diseased by serving in hot or unhealthy climates. The trial was successful and the mineral water was shown to be a powerful tonic, effective where other preparations of iron had failed (Lemprière, 1812). Prospects for the water seemed good and Waterworth's letter to Lemprière lists 28 individuals who had agreed to form an association, under the name of the Sandrocks Spring Society, to promote the spring (Lemprière, 1812).

It would seem that attempts at promotion were successful as, immediately, local guidebooks began to mention the spring and extol its virtues (e.g. Cooke, 1813), although, it was pointed out that there was no carriage road over the uneven ground of the landslip, nor even a footpath. The latter problem seems to have been solved during 1812 as an advertisement for the Sandrock Spring Hotel in Niton in the Morning Chronicle (a newspaper published in London) of November 14th 1812 claimed that "The new road to the spring is now complete and is rendered accessible to persons of the most delicate health". Within two vears the water was available in London, as the Morning Post (another London newspaper) of Friday May 6th 1814 carried the announcement that "Mr Hawkins No 20 Old Bond St and Mr Duncombe 199 Fleet St beg leave to inform the Public they have just received a fresh supply of the aluminous chalybeate water from the Sandrock Spring in the Isle of Wight".

In a pamphlet, dated August 25 1817 Waterworth himself advertised his spring. In this he referred to the earlier reports, confirming that the water had continued to be administered with success, proving good for indigestion, particularly when induced by occasional acts of intemperance, nervous and hysterical complaints, obstinate diarrhoeas, etc. He emphasised that the beneficial effects were not confined to its internal use but that great benefit had been derived from its use as a lotion. However, perhaps the main reason for his pamphlet was to announce that he had established a dispensary at the spring where the water could be procured and medical assistance obtained and where *"the key of the spring is deposited and a guide is in constant attendance to conduct visitors to the spot"* (Waterworth, 1817, p.14). He also provided guidance on drinking the waters as follows:

- (1) evacuation of the bowels using a mild aperient such as Epsom salts,
- (2) begin with ½ ounce (c. 0.018 l) of spring water diluted with 2 ounces (c. 0.072 l) of pure rain water, repeated twice a day,
- (3) in a few days gradually increase the amount to 2 ounces (c. 0.072 l) of water, diluted as before, three times a day,
- (4) diminish the dilution until it can be taken in its pure state, gradually increasing the amount to 4 ounces (c.0.144 I), taken 4 times a day, making in total one pint (c.0.570 I) in 24 hours.

The dispensary, in the form of a pretty cottage, was built at the end of the carriage road, from where a winding footpath led down to the spring (Figure 2). Known as Sandrock Spring Cottage (Figure 3); it had three sitting rooms, two bedrooms, a kitchen and offices and was also the residence of Waterworth and his family. A visit to the spring must have been an exhilarating experience as the road crossed the very rugged landscape resulting from the oldest dated landslide, and the largest recorded on the island, which had taken place in February 1799, only a few years prior to the discovery of the spring (for a discussion of the landslides see Insole *et al.*, 1998).

Over the next few years local guidebooks mention the chalybeate spring but there is no evidence that its facilities were being developed or enhanced in any way. Thus guidebooks by Bullar (1827), Sheridan (1833), Brettell (1840), Barber (1850) and Nelson (1859) merely repeat the claims of Waterworth and/or the analysis of Marcet. In 1840 the fashionable London doctor, Augustus Bozzi Granville, visited the Isle of Wight, as part of his tour of the inland spas and sea bathing places of



Figure 2. "The Sandrock Chalybeate Spring near Niton, Isle of Wight". Drawn, engraved and published by George Brannon, Wotton, Isle of Wight, June 2nd, 1828. The cross above the arched spring enclosure suggests that the spring was venerated as a holy well. A more substantial footpath from the cottage to the spring is shown on later Brannon engravings.

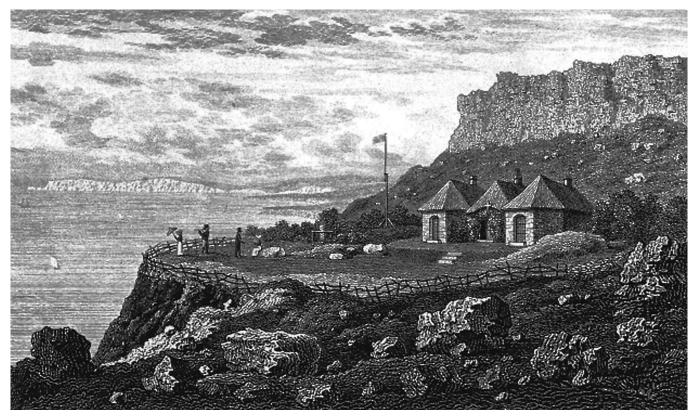


Figure 3. "The Sand-Rock Spring Cottage situated immediately above the aluminous chalybeate spring the property of T. L. Waterworth Esq. about one mile westward of Niton". Drawn, engraved and published by George Brannon, April 1822, London.

England. Amongst other distinctions Granville was a Member of the Geological Society (elected in 1815) and a keen and critical observer. He spoke highly of the Sandrock Spring, situated in the midst of wild and romantic scenery and unique in the country for its strength (Granville, 1841).

According to local newspapers Waterworth died in July 1840 and the following year the cottage and spring were sold at auction. The death of Waterworth seems to have signalled the beginning of the end for the spring. A 1860 guidebook reported that "....the Sandrock Spring is forgotten - the little cottage, erected by the roadside....is passed unnoticed – not one traveller out of a hundred cares to enquire about it...' (Venables, 1860, p.265). The following year Black's guide reported simply that the spring was no longer in use (Black, Most subsequent guidebooks fail to mention the 1861). chalybeate spring at all and, although both the Geological Survey District Memoir (Bristow et al., 1889) and the Water Supply Memoir (Whitaker, 1910) refer to it amongst other chalybeate springs on the island, there is no suggestion that it was in use for therapeutic purposes. Its demise is perhaps not surprising as its main characteristic was its strength. Undiluted it would have been almost undrinkable and the presence of a knowledgeable individual, such as Waterworth, on site was essential for anyone attempting to derive any benefit from drinking the water. An analysis of the spring water was published later in the century (Hehner, 1882) and it may be that some attempt to resurrect use of the spring was made about this time. However, if any attempt was made, it was unsuccessful.

In the 20th Century mass movements in the area of the Undercliff resulted in the loss of all trace of the spring. In September 1928 part of the road to the spring from Niton was carried away by large-scale slip movements. In March 1978 an exceptionally heavy fall of snow, which melted rapidly, followed by about ten days of heavy rain, reactivated old landslides. The resulting movements resulted in the destruction of Sandrock Spring and Sandrock Spring Cottage, as well as a further section of the old road (Insole *et al.*, 1998). Continuing movement and debris falls mean that nothing remains of the once famous 19th Century spring.

Sandrock always retained its title of a spring and does not appear to have ever been considered as a spa. This resulted perhaps from its isolated situation and the lack of any hotel or recreational facilities for patrons. However, some facilities were provided locally at what eventually became the Royal Sandrock Hotel in Niton about 1.5 km to the east of the spring. The early history of the hotel parallels that of the spring and is recorded in a series of documents held by the Isle of Wight Record Office (reference RSN/1 to RSN/45) as well as in local guidebooks and newspapers. A messuage (dwelling house with its outbuildings and land), which became known as Rock Cottage, is described as newly built on the site in January 1794 (RSN/2). A guidebook of 1813 records that "Rock Cottage ... has been (on account of its contiguity to the Sandrock Spring) selected and purchased by Mr Cull of Newport, for the purpose of an hotel. By this means the public will have the advantage of using the water as near as practicable to the fountain head" (Cooke, 1813, p. 85/86). James Cull was a Newport brewer and was one of the individuals who, with Waterworth, had formed the Sandrock Spring Society to promote the spring (Lemprière, 1812).

It would seem that the Sand Rock Spring Hotel, as the new hotel was known, opened during 1812. An advertisement in the Morning Chronicle of November 14th 1812 states that "JAMES MILLS begs to return his acknowledgements to the public for the liberal encouragement he received during the late season. In consequence of the number of the Nobility and Gentry who resorted to the Hotel, he has found it necessary to build large and commodious coach houses and stables, with convenient rooms for servants. In addition to which he intends adding to the number of his bed rooms in the spring for the accommodation of those who may please to honour him with their commands". Mills' name does not appear on any of the legal documents and he may have been a tenant or manager put in by Cull. Probably in 1813 the hotel was extended, as suggested in the above advertisement, with the addition of two new wings. A taphouse (ale-house) was added which, confusingly, was to become known as Rock Cottage.

Over the years the hotel seems to have prospered. Guidebooks began to refer to it as the Sand Rock or Sandrock

Sandrock Spring and Shanklin Spa

Hotel (e.g. Sheridan, 1833) and then as the Royal Sandrock Hotel (Brettell, 1840; Granville, 1841). Princess Victoria had visited the hotel whilst in the Isle of Wight in the early 1830s and the designation Royal may have been assumed soon after her coronation as Queen Victoria on 28 June 1838. The hotel became a coaching inn on the road between Ventnor and Freshwater. It was described by one visitor as "...one of the most picturesque, and, at the same time, most comfortable little country inns in England – a rustic, cottage-looking house, backed by the high cliff under which it seems to shelter; with a woodbine-covered porch, and a sloping lawn, green as an

emerald, bordered with flower beds, and looking out on the English channel..." (Vandenhoff, 1860). It easily survived the demise of the Sandrock Spring, which had provided the impetus for its foundation. Although suffering a setback in 1928, when the road to Blackgang and Freshwater was carried away by a landslip, it continued trading until 1984 when it was terminally damaged in a fire. Three red brick houses now occupy the site and all that remains to remind travellers of the spring and the hotel is a road sign (Figure 4) and Rock Cottage, the old hotel taphouse (Figure 5).



Figure 4. Niton road sign which marks the road which led to the spring. This road now ends at a small carpark and the spring was about 650 m further to the west within the unstable area.



Figure 5. Rock Cottage, the old hotel taphouse, photographed in September 2008 in course of restoration.

SHANKLIN SPA

Following its discovery in the 17th Century it was to be almost 200 years before the chalybeate spring at Shanklin again came to public attention. The spring welled up at the base of cliffs some 60 m below the level of the land on which the town was built. Access down to beach level would have been difficult, discouraging invalids and convalescents who might have been expected to patronise a chalybeate spring. Perhaps, as this lower part of the town was developed in the 19th Century, the spring began to be used but it was not until 1874 that it was mentioned in local newspapers and guidebooks. In June of that year an advertisement appeared in The Standard (a London paper) in which Mr Archibald Hinton announced the opening of the Esplanade Spa Hotel. Over the following years the hotel was variously described as Hinton's Royal Esplanade Hotel and Hinton's Royal Spa Hotel before settling on the title Royal Spa Hotel towards the end of the century. The designation "Royal" seems to have been assumed following a visit by members of the German royal family soon after the hotel opened.

According to Monopole (1903, p.59), Hinton endeavoured to gain public patronage by "opening up a fountain of the water and charging a small sum for admission". He had the water analysed by a Dr. A. H. Hassall, but it failed to gain acceptance from the medical profession. Subsequently he built a reservoir at the rear of the hotel from where he brought water into the hotel and to the Esplanade, where the public could drink it without charge. However, the diameter of the pipes he used was too narrow and they corroded rapidly, so that the water was allowed to run to waste into the sea (Monopole, 1903).

Further development of the spring took place in 1896 following a tour of English spas by the hotel directors, who decided that the plentiful supply of ferruginous water available could be exploited for bathing. Discharge from the spring was constant at around 2000 gallons per day (*c*. 9100 l/d). Initially the spring water was brought into the Winter Garden of the hotel and a small Pump Room erected on the Esplanade facing the Pier. The water was made available to the public and visitors could drink as much as they liked on payment of 1 penny (about £2 on the basis of a comparison of average earnings). The *British Medical Journal* reported that the grandly named Shanklin Royal Chalybeate Spa opened to the public on March 17th 1896 (Anon, 1896). The brief report includes a further analysis by a Professor Attfield which confirmed that the water contained slightly higher concentrations of iron than some of the well-known continental spas.

It was to be some four years before baths were constructed but in its issue of August 18th 1900, The Lancet was able to report that "On August 14th an inaugural gathering was held at which the baths were declared open to the general public as well as to the guests of the hotel" (Anon, 1900a, p. 494). The baths were made at Homburg, in Germany, and water was heated by a system of steam coils identical with those used on the continent. Although on a small scale, this was the first time in Britain that an unstable ferruginous water had been used for treatment in baths and The Lancet's correspondent thought it worthy of encouragement (Anon, 1900a). A longer article was published in the issue of October 6th 1900 describing the layout of the baths in more detail and giving a further analysis of the water made in The Lancet laboratory (Anon, 1900b; Monopole, 1903). Plans show that there were four brass baths used for chalybeate water and two deep baths modelled on those used at major hydropathic resorts such as Bath and Harrogate (Anon, 1900b). The early accounts imply that these were to be increased but there is no evidence that any extension was ever added.

After 1900 local guidebooks (e.g. Ward Lock, 1915) briefly mention the baths at the Royal Spa Hotel; however, there seems to have been little interest from the medical profession. Bradshaw's *Dictionary of Mineral Waters, Climatic Health Resorts, Sea Baths and Hydropathic Establishments* lists Shanklin, but for its sea bathing not its ferruginous waters (Bradshaw, 1904). Similarly Luke (1919) includes Shanklin as a "Leading Seaside Resort" without mentioning the chalybeate spa. Maybe exploitation of the waters continued until the end of World War I but the austere years which followed would have certainly seen their demise. The Edwardian upper middle classes, with their wealth and leisure, who would have patronised the baths, had by then disappeared and the new holiday makers preferred to bathe in the sea - free of charge. The site of the hotel is now a car park, although the chalybeate spring still discharges water at the base of the cliff, from where it drains to the sea.

HYDROGEOLOGY

The chalybeate springs at both Sandrock and Shanklin arise from the Lower Greensand Group of the Lower Cretaceous which underlies much of the southern part of the island (Figure 1). Along the southern coast the rocks lie on the gently, southwards-dipping limb of the Isle of Wight Monocline. The lowest formation, the Atherfield Clay, reaches a maximum thickness of 55 m and consists predominantly of silty clays, although locally silts and fine sands occur (Insole *et al.*, 1998; Rawson, 2006). Some of these sands might yield water but overall the Atherfield Clay can be considered as a non-aquifer. In the present context its only hydrogeological significance will be to throw out springs at its contact with the overlying sandy rocks, of which three separate formations have been distinguished.

The lowest, the Ferruginous Sands Formation, reaches a maximum thickness of about 134 m, and varies from medium to coarse glauconitic sands to sandy mudrocks which are extensively bioturbated. Eleven local members have been recognised in Chale Bay (Insole et al., 1998) but the formation consists essentially of a series of coarsening-upwards units, from sandy muds to glauconitic sands (Rawson, 2006). At the top of the Ferruginous Sands Formation there is a significant lithological change with the appearance of yellow and white sands, which are often cemented into a sandrock. Known as the Sandrock Formation, this reaches a maximum thickness of about 70 m and, in Chale Bay, consists of four coarsening upwards units, each 15 m or more in thickness. Individual units comprise dark grey glauconitic muds and silts grading up through grey sandy muds and muddy sands into medium to coarse white quartz sands (Insole et al., 1998). The overlying Carstone Formation, with a maximum thickness of 22 m. consists of ferruginous, medium- to coarse-grained sandstones with occasional thin beds of conglomerate.

The three sandy formations are considered together as the Lower Greensand aquifer in which flow is predominantly intergranular although fractures are developed in places (Entec, 2008). The aquifer behaves as a layered system, with the layering controlled by formational boundaries, prominent bedding planes and mud horizons. The layering is reportedly so well developed that semi-confined conditions can be present. However, uncertainty remains over the degree of interconnectivity or isolation between different hydrogeological layers (Entec, 2008). As a result of the layering springs are common with water, usually chalybeate, discharging at various levels in the cliffs and along the sides of valleys.

Overlying the three sandy formations is about 30 m of Gault Clay, a rather monotonous sequence of dark blue-grey silty muds (Insole *et al.*, 1998). The Gault is an aquiclude which separates the Lower Greensand Aquifer from the overlying Upper Greensand and Chalk.

The Sandrock Spring discharges from the upper part of the Sandrock Formation. Although, no longer exposed, a section near the spring was measured in the 19th Century (Bristow *et al.*, 1889). The total thickness of the section was 56.1 m and the spring was thrown out by a bed of laminated sand and clay, the upper surface of which was some 12.6 m below the top of the section. According to Berger (in Marcet, 1811, p.216) it issued from a bed of loose quartzose sand containing iron oxide, the sand alternating with thin layers of *"purplish argillaceous slate"*. Above this lay a bluish calcareous marl, several fathoms in thickness (one fathom is about 1.8 m), which contained embedded nodules of iron sulphide. Many of these nodules

were partially decomposed and Berger supposed that this decomposition accounted for the principal ingredients of the spring. The spring was visited also by Michael Faraday whilst on a family holiday in Niton during 1824 (Bowers and Bowers, 1996). Faraday had a passing interest in geology and had joined the Geological Society that same year. In his notebooks he records *"The iron sand sometimes full of pyrites and affording solutions of sulphates of iron and alumini. Sand rock spring is one of these"* (Bowers and Bowers, 1996). Faraday also noted that many of the sandstones were hard and cherty with a siliceous cement and that he found a vein of chalcedony in the sandstones.

In contrast to Sandrock, the spring which provided the water to the baths at the Royal Spa Hotel in Shanklin was derived from a dark loamy greensand, about 7.6 m in thickness, in the middle part of the Ferruginous Sands Formation. Many of the beds within this formation consist largely of polished grains of brown siderite or ferruginous calcite, and are often oolitic (Osborne Wight, 1921). The glauconite in the sands has been subjected to chemical weathering resulting in alteration to iron oxides, hydroxides and carbonates.

HYDROCHEMISTRY

The available analytical data for both springs are shown in Table 1. The analysis of Sandrock Spring by Marcet and those of Shanklin Spa by Hassell and The Lancet are all reported in terms of a hypothetical mixture of salts, which if dissolved in water, would produce the observed hydrochemistry. The result is artificial and for example Marcet (1811) assumed that aluminium was present as crystalline alum, although no potassium was found. Scudamore (1820) recalculated Marcet's analysis emphasising the difficulty in interpreting the data and Whitaker (1910) recalculated the analysis on the assumption that aluminium was present as aluminium sulphate. Hehner (1882) also recalculated Marcet's figures and his results have been used in the present paper so that a direct comparison can be made with his own data. In Table 1 all analyses have been broken down into individual ions to conform to modern practice. However, analytical chemistry was in its infancy in 1811 and, although improvements took place during the rest of

the 19th Century, the results should be taken as an indication of the general chemistry of the groundwaters, for comparing the two sources, rather than paying too much attention to variations in individual values at a particular source. Gaps in the table indicate that no data are reported for that particular species. This may be because no analysis was attempted or it was not detected. Unfortunately no pH values were determined by the early analysts.

Table 1 also includes the concentration ranges of various species measured at nine monitoring points within the Isle of Wight Lower Greensand Groundwater Body (Entec, 2008). These are presented in the form minimum concentration/mean/maximum concentration in mg/l (e.g. for Fe this is .003/2.5/44). Entec (2008) reported Fe and Mn as both total and dissolved concentrations. The ranges given in Table 1 are of total concentrations, on the basis that these are what are likely to have been determined in the historic analyses. Total Fe concentrations were found to be approximately twice dissolved Fe concentrations and total Mn concentrations were greater than dissolved Mn concentrations by about 10% (Entec, 2008).

The data show that there are major differences in the hydrochemistry of the two chalybeate springs. The Shanklin Spa water lies within the range recorded for the monitoring points within the Isle of Wight Lower Greensand Groundwater Body whereas, with the sole exception of Mn, concentrations of individual species at Sandrock Spring are well outside this range. The very high concentrations of Fe and Al stand out and Marcet (1811) considered no chalybeate or aluminous spring in the chemical history of mineral waters compared, in regard to strength, with the Sandrock water.

DISCUSSION

The rocks of the Lower Greensand Group are rich in glauconite, a green illite-related mineral from which they derive their name. Glauconites contain both Fe(III) and Fe(II) and probably form in a moderately reducing environment. Thus they are frequently associated with pyrite and such an association occurs within the Lower Greensand. Oxidation of pyrite in the unsaturated zone, with dissolved O_2 as the

| | Sandrock 1 Marcet 1811 | Sandrock 2 Hehner 1882 | Shanklin 1 Hassell c 1874 | Shanklin 2 Attfield 1896 | Shanklin 3 The Lancet 1900 | |
|------------------|------------------------------|------------------------------|---------------------------------|--------------------------------|----------------------------------|-------------|
| Species | 1011 | 1002 | C 10/4 | 1890 | 1900 | Range |
| Na | 551 | 139 | 22 | 32 | 45 | 9/19/53 |
| K | | 19 | 3 | 6 | 5 | 1.2/3.2/6.3 |
| Ca | 335 | 293 | 58 | 62 | 63 | 27/82/146 |
| Mg | 50 | 88 | 15 | 4 | 3 | 2.1/6.8/11 |
| Fe | 1193 | 1141 | 15 | 33 | 20 | .003/2.5/44 |
| Al | 259 | 614 | | 0.56 | | .0015/-/.66 |
| Mn | | 0.4 | | | | .0005/.1/.5 |
| Ni | | 7.7 | | | | .0001/-/.02 |
| HCO ₃ | | | 215 | 177 | 162 | 61/238/379 |
| SO_4 | 5092 | 6369 | 46 | 62 | 59 | 6/30/89 |
| Cl | 346 | 220 | 37 | 70 | 81 | 20/34/65 |
| SiO ₂ | 100 | 92 | 20 | 27 | 29 | 2.3/10/23 |

Table 1. Published analyses of the waters of Sandrock Spring and Shanklin Spa together with the concentration ranges of various species from nine monitoring points within the Isle of Wight Lower Greensand Groundwater Body taken from Entec (2008). All concentrations are expressed as mg/l.

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oxidising agent proceeds in two steps (Appelo and Postma, 1996), according to the reactions:

1.
$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_{4^2} + 2H^+$$

and 2

.
$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + 2H^2$$

At depth within the saturated zone, groundwater will be isolated from the atmosphere and dissolved O2 will be rapidly consumed. Step 2 may be inhibited leading to incomplete pyrite oxidation resulting in highly acidic solutions rich in SO4² and Fe2+. In rocks containing calcite the acidity is neutralised by the association of protons (H^+) with the carbonate ion (CO_3^{2-}) to form bicarbonate (HCO3⁻). However, where carbonates are absent or decalcification has occurred, pH can remain low resulting in reactive groundwaters which in turn can result in the enhanced dissolution of minerals such as glauconite and kaolinite in the sandy mudrocks.

The dissolution of kaolinite can be represented by the equation (Appelo and Postma, 1996):

$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O$

The concentration of Al3+ is extremely low at the near neutral pH characteristic of most groundwaters. However, acid conditions may bring considerable amounts of aluminium into solution, particularly in groundwater with a pH below 4 and concentrations of several thousand mg/l $\widehat{Al}^{\scriptscriptstyle 3+}$ have been recorded (Hem, 1989). In sediments aluminium brought into solution in this way would normally be adsorbed by exchange with cations such as Ca2+, Mg2+ and Na+ but might be expected to reach high concentrations if cation exchange sites were not available.

The above discussion shows, that in non-carbonate-bearing rocks, it is possible to generate groundwaters with enhanced concentrations of both iron and aluminium. It is suggested that such conditions are found in certain units within the Sandrock Formation of the Lower Greensand where beds of slightly coherent white and yellow quartz sands up to about 8 m in thickness occur. The absence of carbonate and clay minerals within the pure quartz sands and the localised confined or semi-confined conditions combine to provide an environment for the development of reduced acid groundwater carrying iron and aluminium in solution. The groundwater is also enriched in nickel, but manganese concentrations, which might be expected to follow iron, remain low. The high concentrations of sodium, magnesium and chloride suggest a mature groundwater in which there has been plenty of time for water rock interaction to take place.

The geochemistry of the water of Shanklin Spa is rather different to that of the Sandrock Spring and there is little to distinguish this water from that found elsewhere within the Isle of Wight Lower Greensand, although iron concentrations are in the upper part of the recorded range (Table 1). There are three sources of iron in the Ferruginous Sands; the weathering and oxidation of pyrite, the breakdown of glauconite and the solution of siderite or ferruginous calcite. The chemistry of individual springs is likely to vary, depending on the mineralogy of the beds from which they arise, resulting in large variations in iron concentrations. This is confirmed by the work of Entec (2008) who found large variations in iron concentrations between individual sources within the groundwater body, although concentrations at individual sampling points remained consistent.

Shanklin Spa was supplied from a reddish bed of ironsand which became pebbly in its upper part (Osborne Wight, 1921). The pebbles were composed of green-stained quartz, sandstone and other siliceous rocks and the impression is given that the bed was dominated by quartz sands rather than carbonate sands. It is suggested that the spa water originated from ironrich sands, poor in carbonate, where groundwater pH was lowered to around 6.5 to 6.2 maintaining a significant concentration of Fe2+ in solution. However, unlike the water of

Sandrock Spring, bicarbonate is still present although at concentrations well below the mean concentration for the Isle of Wight Lower Greensand Groundwater Body (Table 1). Elevated chloride concentrations, above the maximum of the Entec range, suggest some intrusion of seawater; not surprising considering the position of the spa at the base of coastal cliffs.

Sandrock Spring and Shanklin Spa are both chalybeate springs but have vastly different hydrochemistries. The Sandrock water is strongly acidic contains no bicarbonate and the anion chemistry is dominated by sulphate. Such mineral waters were termed "vitriolated chalvbeates" by spa physicians (e.g. Saunders, 1800) and were relatively rare in England. The Shanklin water is weakly acidic and bicarbonate is the dominant anion, giving the name "carbonated chalybeates" to these waters. Such waters were not uncommon in England and included those at Tunbridge Wells and London spas such as Sadlers Wells and Islington.

Marcet's analysis of the Sandrock water showed that each pint contained 107.4 grains of solid matter, equivalent to around 12 300 mg/l of total dissolved solids. At this time two other waters of the same type were being prescribed by physicians; those from Hartfell, near Moffat in southern Scotland, and Horley-Green near Halifax in Yorkshire. With total dissolved solids concentrations of about 700 mg/l, at Hartfell (Horsburgh, 1754) and about 5700 mg/l at Horley-Green (Garnett, 1790), both waters were considerably weaker than that from Sandrock, justifying claims for the uniqueness of the Sandrock water. Marcet felt that, in contrast to many medicinal waters, at Sandrock the water contained "rather a redundance than a deficiency of power" (Marcet, 1811, p247) and certainly with its inky colour and bitter taste it would have been a challenging liquid to drink!

Around 1880, another vitriolated chalybeate was identified at Flitwick in Bedfordshire (Key, 1968). With a total dissolved solids concentration of about 4760 mg/l, and iron, aluminium and copper concentrations of 770, 2.3 and 6.0 mg/l respectively (Woodward and Thompson, 1909), this was again considerably weaker than the Sandrock water. However, as with the Sandrock Spring it was derived from sands within the Lower Greensand Formation, although some of the iron may have been derived from overlying peat.

Chalybeate waters were notoriously unstable because of the oxidation of Fe2+ in solution and the precipitation of Fe(OH)3. This meant that the waters did not travel well, leading to the requirement that they should be consumed close to their source. However, by the beginning of the 19th Century, chemists and physicians had recognised that carbonated chalybeates were more readily decomposed than vitriolated chalybeates. The reason for this can be demonstrated by the following equations:

A.
$$Fe^{2+} + 1/4O_2 + 5/2H_2O \leftrightarrow Fe(OH)_3 + 2H^2$$

and

$Fe^{2+} + 2HCO_3 + H_2O \leftrightarrow Fe(OH)_3 + 2CO_{2 (gas)} + H^+$ В

In the case of the vitriolated chalybeates (equation A) precipitation of ferrous hydroxide could be restricted by the exclusion of oxygen. This could be achieved to some extent by good corking and placing bottles on their side. Using such methods it was possible to transport bottles of the Sandrock water as far as India, where it was apparently held in considerable repute (Waterworth, 1817). With the carbonated chalybeates ferric hydroxide was precipitated as a result of the loss of carbon dioxide gas (equation B). Even if the water was bottled at source, the build up in the pressure of carbon dioxide within the bottle meant that it was almost impossible to prevent its slow release and the formation of a brown precipitate making the water unpalatable. For this reason the rarer vitriolated chalybeates, such as that at Sandrock, were regarded as more valuable than the commoner carbonated waters.

CONCLUSIONS

Two chalybeate springs on the Isle of Wight were patronised for limited periods during the 19th and early 20th centuries. The Sandrock Spring, near Niton, although yielding a water much valued by spa physicians, had high concentrations of both iron and aluminium and the maximum recommended intake was only a pint a day, even for experienced drinkers. The death of its owner in 1840 seems to have marked the beginning of the end for the spring which was first cut off and finally destroyed by a series of landslips in the 20th Century. The strength of the water probably contributed to its demise as, without supervision, it would have been undrinkable to casual patrons.

The iron concentration of the spring which supplied Shanklin Spa was two orders of magnitude less than that of Sandrock and the water was used for drinking and bathing. The baths, opened in 1900, were the first in Britain to use heated chalybeate waters and perhaps enjoyed some initial success. However, there seems to have been no sustained interest from the medical profession and the baths may have been disused by World War 1.

Although both springs were described as chalybeate there were major differences in their hydrochemistry. The Sandrock water was a *"vitriolated chalybeate"* in which sulphate was the dominant anion and Shanklin water a *"carbonated chalybeate"* in which bicarbonate was dominant. The former precipitated iron by the *"absorption of oxygen"* and the latter by the *"loss of carbonic acid"* (Saunders, 1800, p.58). Because of this the Sandrock water was the more stable and could be sent to London and beyond *"provided the atmospheric air be carefully excluded by good corking and the bottles be placed on their side in a cool apartment"* (Lemprière, 1812, p.34).

Differences in the hydrochemistry of the two springs are related to their mineralogy. The Sandrock Formation which was the source of the Sandrock spring is a clean quartz sand without accessory silicate or carbonate minerals or cements. Water-rock interaction, involving the oxidation of pyrite, resulted in a groundwater with a pH below 4.5, in which bicarbonate was absent, and which could hold high concentrations of iron and aluminium in solution. The Ferruginous Sands Formation, the source rock for the water supply to Shanklin Spa, contains variable amounts of glauconite and other clay minerals as well as quartz and carbonate sands. Some intervals are rich in carbonate, resulting in high groundwater bicarbonate concentrations, a neutral pH and low iron concentrations. Other intervals, including the source of the spa water, are quartz sands, depleted in carbonate minerals. Here some bicarbonate will be produced by the weathering of silicate minerals, but groundwater bicarbonate concentrations are generally low, with a pH between 6.2 and 6.5, and up to 40 mg/l of iron in solution.

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