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Hyperalkaline groundwaters and tectonism in the Philippines: significance to natural Carbon Capture and Sequestration

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Abstract

The potential of using ophiolites for CCS has been pointed out before, but no case study has been conducted for the Philippines. Here, the potential for CCS in both ophiolites in general and ophiolites in the Philippines in particular is examined and discussed. Specific drawbacks of using ophiolites as a CO_2 sink are presented for the first time, using information from natural analogue studies in the Philippines and Jordan.

Keywords: hyperalkaline groundwaters; ophiolite; seismic activity

Introduction

With a growing population, up from 76.6 million in 2000 to 88.6 million in 2007 and a projected 92.3 million in 2009 [1], energy requirements in the Philippines are soaring. In 2006, electricity generation was an estimated 47 billion kWh [2] producing some 80 million tonnes of CO_2, a value that is likely to rise as the population continue to grow. Electrical energy consumption has been increasing at some 3% per annum, leading to shortages in some parts of the country and regular brown outs in others as investment in new power plant build lags consumption. New build has focussed on thermal power plants, ensuring that CO_2 production will continue to grow and research is now turning to potential forms of carbon capture and sequestration (CCS) in the Philippines. To date, focus has been on hydrocarbon fields that are nearing the end of their useful life or are considered dry wells [3, 4, 5], but there could be even greater potential in the many ophiolites spread across the country. In both cases, extensive site characterization must be undertaken to include reservoir characteristics, geochemical and hydrogeological simulations on CO_2 reaction with the host rock and groundwater among others.

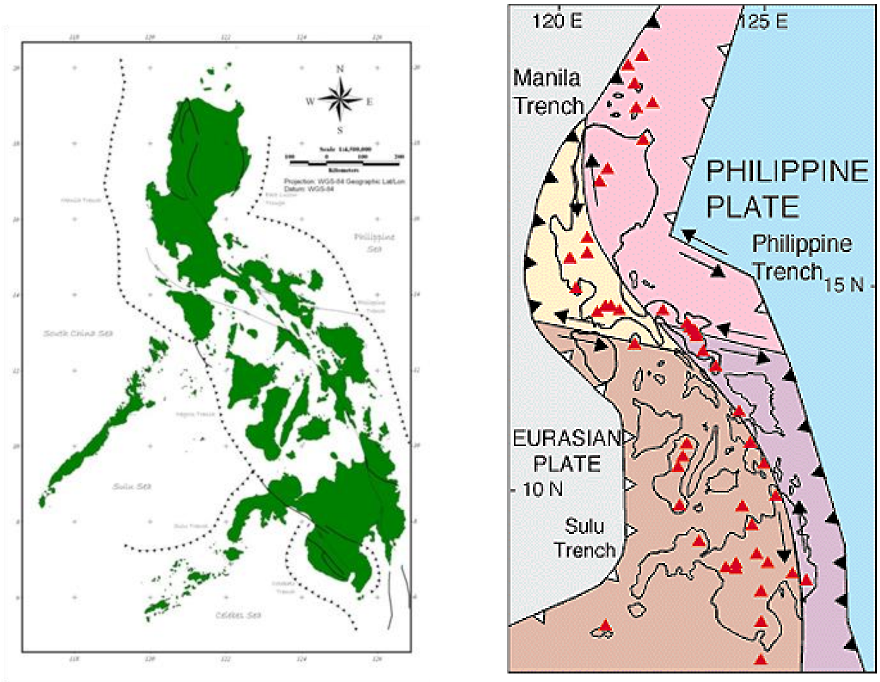

Figure 1: The complex geology of the Philippines is a result of the collision of several tectonic plates [6,7].

The geology of the Philippines archipelago is particularly complex, resting as it does at the boundary of several tectonic plates (see Figure 1). Given this geological scenario, CCS in the Philippines becomes slightly more complicated than is normally the case. Major complications that would affect any CCS programme include the high degree of tectonic activity, high geothermal gradient (brought by the very long Philippine Fault that transects the whole archipelago) and the number of active volcanoes (Figure 1). Despite the fact that it appears unlikely that the Philippines could meet the site selection criteria outlined by the IEAGHG [e.g. 4, 5], this does not rule out the country becoming a test bed for technologies that could lead to more appropriate implementation of CCS in the Asia-Pacific ring-of-fire region.

One side effect of this is the presence of widepread ophiolites, with at least 20 significant bodies described to date, distributed across the entire country (Figure 2). Ophiolites, as defined here, adapt the nomenclature of the Penrose Conference of 1972 [10] and, from top to bottom, consists of the following lithologies (see also Figure 3):

deep (abyssal) marine sediments
pillow lavas (basalt)
sheeted dyke complex
high level/isotropic gabbro
layered mafic cumulates (gabbro)
layered ultramafic cumulates
transition zone dunites and residual peridotites

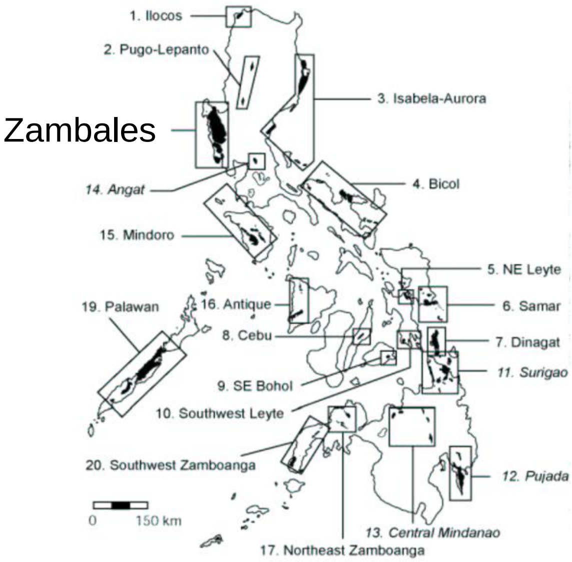

Figure 2: Distribution of ophiolites in the Philippines [8,9].

As has previously been reported [11], ophiolites could be efficient zones for CCS. The authors estimated that $\approx 10^4$ to 10^5 tons per year of atmospheric CO_2 are converted to solid carbonate minerals via peridotite weathering in Oman. They further noted that ophiolite CCS could be accelerated by injection of CO_2 at elevated pressure and temperature and could consume >1 billion tons of CO_2 per year in Oman alone, affording a low-cost, safe, and permanent method to capture and store atmospheric CO_2.

Mechanism of potential carbon sequestration

All ophiolites are characterised by the presence of hyperalkaline groundwaters. The hyperalkaline pH values (generally between pH10 and 11, but up to pH12 has been reported [12]) observed in the groundwaters are a product of the serpentinisation of the ophiolites, a reaction which has several possible pathways with the exact reaction pathway depending on Mg content of the precursor olivine/pyroxene or serpentine product, CO_2 fugacity, water-rock ratio, Ca^{2+} content of groundwater, etc.

When considering the origin of the hyperalkaline groundwaters at most ophiolites, two processes generally need to be considered:

- high to medium temperature alteration
- low temperature precipitation

The former often shows itself in the form of pervasive serpentinisation of the entire mantle sequence and is presumed to be pre- or syn-tectonic. This hydrothermal alteration may be characterised by the reaction:

$$6Mg_2SiO_4 + Mg_3Si_4O_{10}(OH)_2 + 9H_2O \rightarrow 5Mg_3Si_2O_5(OH)_4 \quad (1)$$

forsterite talc serpentine

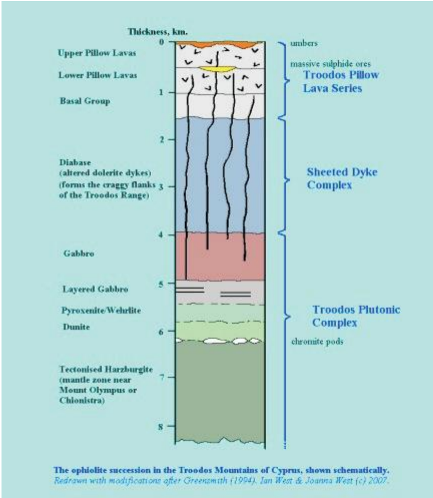

Figure 3: Example of typical ophiolite stratigraphy from the Troodos ophiolite in Cyprus [13]

which fixes the upper temperature of serpentine formation at 500°C. Of more relevance to the conditions of meteoric groundwater circulation of interest here is low temperature serpentinisation. In this case, $Mg(HCO_3)_2$-type meteoric groundwaters react with the ultramafic rocks of the ophiolite in an essentially open system and produce $Ca(OH)_2$-type (spring) waters. The partial reactions may be expressed as (but see also alternatives in [14]):

olivine dissolution

$$3H_2O + 2\ Mg_2SiO_4 \rightarrow 5Mg_3Si_2O_5(OH)_4 + Mg^{2+} + 2OH^- \qquad (2)$$

forsterite serpentine

$$2H_2O + Fe_2SiO_4 \rightarrow 2Fe(OH)_2 + SiO_2 \qquad (3)$$

Fayalite

pyroxene dissolution

$$2H_2O + 3MgSiO_3 \rightarrow Mg_3Si_2O_5(OH)_4 + SiO_2 \qquad (4)$$

$$H_2O + FeSiO_3 \rightarrow Fe(OH)_2 + SiO_2 \qquad (5)$$

$$H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2OH^- + SiO_2 \qquad (6)$$

precipitation

$$3(Mg^{2+} + 2OH^-) + 2SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + H_2O \qquad (7)$$

along with the groundwater components:

$$Mg^{2+} + HCO_3^- + OH^- \rightarrow MgCO_3 + H_2O \qquad (8)$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \qquad (9)$$

Of course, without full petrological details and kinetic information, the total reaction equation is always indeterminate and ignores the potential catalytic role of microorganisms that have been found in hyperalkaline springs present in ophiolites systems [15]. Nevertheless, from the viewpoint of CCS, it is worth noting that:

- the fluid output contains low Mg and SiO_2, regardless of the input water chemistry, so they are conserved within the system
- equation 7 involves a balance between Mg (from equation 2) and the input groundwater, with SiO_2 derived from equations 3 to 6 – so serpentine precipitation is buffered by differential olivine-pyroxene dissolution
- hydroxide is produced in equations 2, 3, 5 and 6, but the (Mg^{2+} + $2OH^-$) of equation 2 is consumed in equation 7, leaving only Ca and Fe sources, with Ca likely to dominate based on the source mineralogy
- any CO_2 injected into an ophiolite groundwater would be consumed in equations 8 and 9, giving rise to aragonitic to dolomitic secondary carbonates within the ophiolite

Under natural conditions, the groundwater pH remains high until it is buffered by atmospheric CO_2 at or near the ground surface. This usually leads to impressive tufa (amorphous calcium carbonate) deposits at springs or along nearby river courses (e.g. Figure 4).

Figure 4: Massive tufa deposits on a stream in the Zambales ophiolite, Philippines [16].

Of immediate relevance to CCS in the Philippines is the fact that new thermal power plant build could easily be focussed on the known ophiolites (for example, two are within easy reach of the capital, Manila – see Figure 2) and their natural ability to consume CO_2 could be utilised by pumping CO_2 captured from flue gases directly into the ophiolites. This could offer a relatively cheap form of CCS of direct relevance to a rapidly industrialising developing nation such as the Philippines.

Potential drawbacks

As far as the authors are aware, drawbacks of utilising the hyperalkaline groundwaters of ophiolites have never been addressed and these include:

- high inflammable gas (H_2, CH_4) concentrations in the groundwaters [e.g. 12, 17], with attendant danger of explosion
- high water temperatures [e.g. 18], meaning resource competition could be an issue. For example, numerous hyperalkaline groundwater springs in the Philippines are already utilised as thermal baths [e.g. 19]
- rapid groundwater flowpath clogging or sealing by tufa

Of these three, the first could be minimised by appropriate operational procedures and the second by ensuring a significant exclusion zone around existing thermal bath facilities (although this would not necessarily rule out stakeholder resistance; cf. [20]). However, groundwater flow path clogging is difficult to avoid.

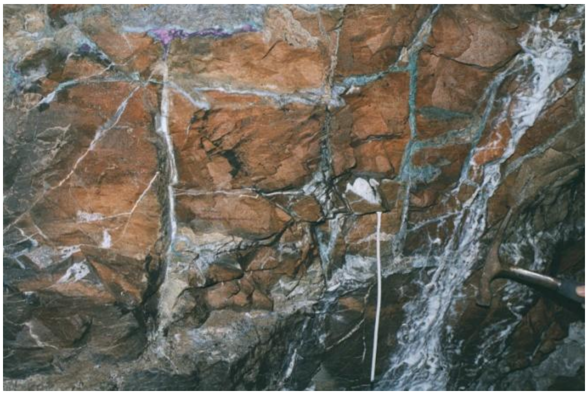

Figure 5: typical clogging of hyperalkaline groundwater flowpaths in the Bituminous Marl Formation of northern Jordan [26]. Note geological hammer, bottom right, for scale.

In the hyperalkaline groundwater system of northern Jordan (produced by leaching of natural concretes; see [21] for details), sealing of the groundwater flow paths is ubiquitous. Near-surface, the mechanism is similar to that observed in the Philippines (and other ophiolites: cf. [12, 22]) with atmospheric CO_2 uptake inducing tufa deposition (in spectacular cases, tufa thicknesses of up to 15 m have been reported [23]). At depth, it appears that interaction of the hyperalkaline groundwaters with HCO_3^- in the rock porewaters is enough to induce pathway clogging, at least in small aperture fractures (see Figure 5). Although other reactions also come into play in the flowpaths in Jordan (see details in [24, 25] and references therein), this mechanism is analogous to what would be expected in the hyperalkaline groundwater pathways in an ophiolite being utilised for CCS and it is therefore expected that any such groundwater system will effectively self-seal.

Implications for CCS in ophiolites

In Jordan, the sealed fractures have been shown to be highly stable, with the fracture sealing material at least several hundred thousand years old and suggestions that some could be up to 2 million years old [27, 28]. This is understandable insofar that, once sealed, there is no obvious way for the hyperalkaline groundwater to flow along the same fracture network and so it must seek alternative pathways (see also comments in [25]).

The implications for CCS in ophiolites in general is that they may not actually be as efficient in hyperalkaline groundwater systems as suggested in [11] and elsewhere. Clearly, CO_2 could be pumped into the ground at ever greater pressures, but this could rapidly become too costly to sustain. In addition, because it would be all but impossible to predict where the hyperalkaline groundwaters would flow once the original flowpaths had clogged (cf. comments in [25, 29]), it would be difficult indeed to convince stakeholders that the risk to their local thermal bath would be low.

However, there is at least one mechanism which might at least minimise such uncertainties. Looking to Jordan, once again, on the northern border with Syria, the River Yarmouk flows in a very steep-sided channel (Figure 6) westwards to the River Jordan. Near the village of Maqarin, it has been shown that the valley sides are so steep that gravitational tectonics (i.e. collapse of the steep valley walls) allows the rock to de-stress, to at least several 100s of metres behind the valley walls. This repeatedly re-opens the previously sealed groundwater flowpaths, so allowing further reaction between the hyperalkaline groundwaters and porewater HCO_3^- or atmospheric CO_2 [25, 28, 31]. This cycle can be repeated time and time again, so acting as a relatively efficient trap for CO_2.

Figure 6: The steep-sided valley of the River Yarmouk near Maqarin in northern Jordan [30]. The photographer is standing in Jordan, looking north to Syria on the opposite side of the valley.

Obviously, such an esoteric mechanism is likely to have little application to the vast majority of ophiolites around the world, but there is a direct analogy in the case of the Philippines: as shown in Figure 1, the Philippines lies in a tectonically complex area of the earth's crust and is also prone to many earthquakes (Figure 7). This makes it possible that ophiolites in the Philippines could nevertheless still be utilised for CCS. Obviously, this needs to be examined in greater depth, looking, for example, at historical records of the longevity of hyperalkaline springs and comparing those in tectonically quiescent areas with those in active zones. Only then could it be shown that tectonic re-activation of tufa-sealed systems is a mechanism of relevance to CCS in the Philippines.

Conclusions

Ophiolites have been proposed as potential sites for CCS facilities and, at first sight, they certainly appear promising with the capacity of the Ca-rich, hyperalkaline groundwaters to soak up large volumes of CO_2 by carbonate precipitation. Unfortunately, evidence from natural analogue studies in Jordan (and the Philippines) suggest that groundwater flowpath self-sealing (with secondary carbonates) is likely to disrupt the original site hydrogeological conditions, leading to rapid pore clogging. Interestingly, in tectonically active zones such as the Philippines, constant movement could repeatedly re-open sealed porosity, so allowing further reaction between the hyperalkaline groundwaters and CO_2. The full implications of this mechanism have still to be quantitatively assessed, but this would be possible by dating both sealed fractures in Jordan and assessing the longevity of hyperalkaline springs in the Philippines.

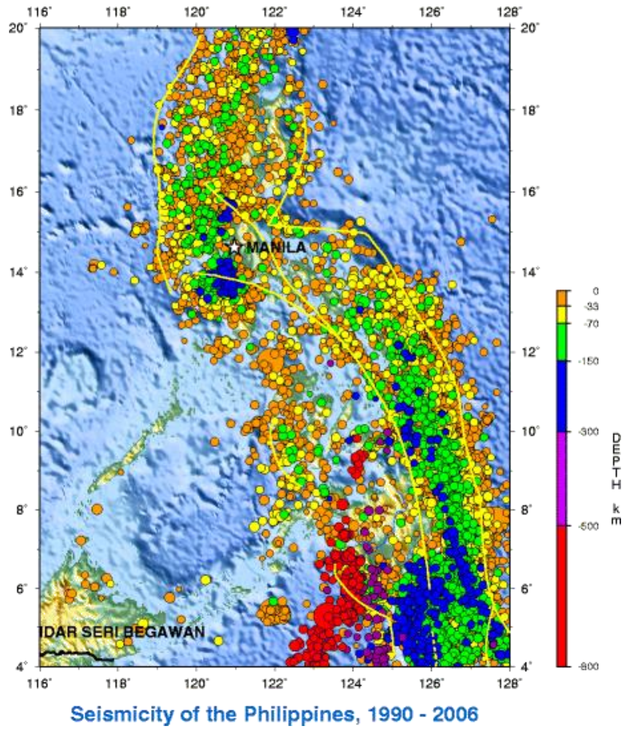

Figure 7: Plots of earthquake focii and their corresponding depths [32]

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