Geological, geochemical and social-scientific assessment of basaltic aquifers as potential storage sites for CO₂

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Basaltic aquifers have the potential to provide secure option for CO_2 sequestration. Because basaltic rocks are widely distributed around the world, their capacity for storage of anthropogenic CO_2 emissions is enormous. In addition, geochemical trapping of CO_2 injected into basaltic aquifers occurs quickly, because basaltic rocks contain many cations that react with CO_2 to form stable carbonate minerals. Two types of large-scale basaltic aquifers may be suitable for sequestering huge amounts of anthropogenic CO_2 : continental flood basalt aquifers and deep-sea basalt aquifers. Here, we assess the potential of these two CO_2 sequestration options from geological, geochemical and social-scientific perspectives.

From a geological and geochemical viewpoint, both continental flood basalt and deep-sea basalt aquifers have excellent CO_2 storage potential. In deep-sea basalt aquifers, however, storage of injected CO_2 may be more secure than in continental flood basalt aquifers, because leakage of CO_2 to the atmosphere is minimized by geological, geochemical and physical barriers associated with the deep-sea environment. In addition, from a social-scientific point of view, several current CO_2 injection projects in continental flood basalts have encountered problems due to groundwater depletion, and large-scale implementation of CO_2 storage in continental flood basalt aquifers might cause contamination of freshwater resources needed for domestic and agricultural use. In striking contrast to continental flood basalts, deep-sea basalts can be used for CO_2 storage without encountering critical problems, because deep-sea basalt aquifers have no economic value. We conclude, therefore, that deep-sea basalt aquifers are a better option for CO_2 storage than continental flood basalt aquifers.

Keywords: CCS, basaltic aquifer, deep-sea basalt, groundwater depletion, water pollution

INTRODUCTION

Recognition of the diverse effects of global warming in recent decades has led to the expectation that largescale implementation of CO_2 capture and storage technologies will be an important component of efforts to reduce industrial CO_2 emissions (IPCC, 2005). Many studies have investigated CO_2 storage in deep aquifers, which are distributed worldwide and have a large potential storage capacity. Several experimental and commercial CO_2 injection projects have already been implemented (Kongsjorden *et al.*, 1997; Kharaka *et al.*, 2006), and no known engineering problems would prevent large-scale implementation of CO_2 storage in such aquifers. The greatest remaining need is to ensure storage security. During CO_2 sequestration in deep aquifers, the captured CO_2 is typically injected into a formation at depths of more than 800 m, where pressure and temperature are above the critical point of CO_2 (31.1°C, 7.38 MPa) (Bachu, 2002). Because supercritical fluids are highly mobile, however, the injected CO_2 might flow in the aquifer and CO_2 might leak to the surface. Storage security therefore depends on restricting CO_2 flow in the storage aquifer.

Injected CO_2 can be trapped by either physical or geochemical trapping mechanisms. Structural/ stratigraphic, gravitational, and residual gas trapping are physical mechanisms. In structural/stratigraphic trapping injected CO_2 is stored as a gas, liquid, or supercritical

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Fig. 1. (a) Phase diagram of the CO_2-H_2O system (modified from Diamond and Akinfiev, 2003). (b) CO_2 density as a function of temperature and pressure (modified from Bachu, 2003). In panel (a), "ice" and "water" represent the solid and liquid phases of H_2O , respectively, and "c-h", "liquid", and "vapor" represent CO_2 clathrate hydrate, CO_2 liquid and CO_2 vapor, respectively. The conditions in a deep-sea basalt aquifer (injection target) at the stop point (see text) and at the seafloor are shown in both panels. Seawater density as a function of sub-seafloor temperature and the corresponding sub-seafloor pressure are also shown in panel (b). Density calculations for seawater are based on UNESCO (1983) under the assumptions that seafloor depth is 3200 m and the thickness of the overlying sediment is 300 m.

fluid beneath a low-permeability caprock (Bachu *et al.*, 1994; IPCC, 2005). This is the dominant trapping mechanism during the period immediately after injection of CO_2 . Gravitational trapping typically occurs in deep-ocean sediments, because liquid CO_2 is denser than the surrounding aquifer water in the high-pressure, low-temperature conditions of that environment (Levine *et al.*, 2007) (Fig. 1). Residual gas trapping, in which interfacial tension causes CO_2 bubbles to be trapped in small pore spaces (Suekane *et al.*, 2008), is currently considered one of the most important physical trapping mechanisms. These physical trapping mechanisms mainly provide short-term CO_2 storage security.

In contrast to physical trapping mechanisms, geochemical trapping mechanisms, which rely on chemical reactions among CO_2 , water and host rock are more important for long-term CO_2 storage security. Geochemical trapping proceeds according to the following simplified reactions:

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \to \mathrm{HCO}_3^- + \mathrm{H}^+ \tag{1}$$

$$(Ca,Mg,Fe)^{2+} + HCO_3^- \rightarrow (Ca,Mg,Fe)CO_3 + H^+$$
 (2)

$$(K,Na)_{x}(Ca,Mg,Fe)_{y}Si_{3}AlO_{8} + (x + 2y + 3)H^{+} + 4H_{2}O \rightarrow x(K,Na)^{+} + y(Ca,Mg,Fe)^{2+} + 3H_{4}SiO_{4} + Al^{3+}.$$
 (3)

In an aquifer, injected CO₂ gradually dissolves into the aquifer water (solubility trapping: Eq. (1)) and then forms carbonate minerals (mineral trapping: Eq. (2)) by chemical reactions with alkaline-earth elements eluted from the host rock (host-rock dissolution: Eq. (3)) (McGrail et al., 2006). Host-rock dissolution (Eq. (3)) controls both the solubility and mineral trapping reactions, by neutralizing the groundwater pH, thus enhancing CO₂ dissolution, and by providing the cations that react with the dissolved CO₂ to form carbonate minerals. Once the CO₂ has dissolved and ionized, the injected CO₂ loses it buoyancy and no longer moves upward; thus, the risk of leakage of the injected CO_2 is decreased. Incorporation of the CO_2 into the mineral phase (carbonate minerals) is the most secure and permanent geological storage method for anthropogenic CO₂. In summary, geochemical trapping is the



Fig. 2. Distribution of continental flood basalts (black polygons) and deep-sea basalts with potential for CO_2 storage (hatched rectangles) (modified from Goldberg and Slagle, 2009; Matter and Kelemen, 2009). Abbreviations: CRBG, Columbia River Basalt Group; EPR, East Pacific Rise; MAR, Mid-Atlantic Ridge; SWIR, Southwest Indian Ridge.

transformation of injected CO_2 (liquid or supercritical phase) into more stable phases (ions and minerals) through reactions with the aquifer water and host rocks.

In the past few decades, the basaltic aquifers have received considerable attention as potential CO_2 storage sites because of the high reactivity and abundant cations of basaltic rocks. In acidic conditions the dissolution rate of basalt is significantly fast compared with other crystalline silicate rocks because the dissolution rates of its main constituent minerals, olivine, pyroxenes and plagioclase (anorthite), are comparatively fast among common rock-forming silicate minerals. The dissolution reactions of these minerals in an acidic environment are as follows (Eq. (1), olivine; Eq. (2), pyroxenes; Eq. (3), anorthite):

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightarrow 2(Mg,Fe)^{2+} + SiO_2 + 2H_2O$$
 (4)

$$(Mg,Fe)_2Si_2O_6 + 4H^+ \rightarrow 2(Mg,Fe)^{2+} + 2SiO_2 + 2H_2O(5)$$

$$CaAl_2Si_2O_8 + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2SiO_2 + 4H_2O.$$
 (6)

It is clear from the chemical compositions of the constituent minerals that basaltic rocks contain abundant divalent cations, especially Mg, Ca and Fe, and they have a high capacity for acid neutralization and stable carbonate mineral formation. Therefore, with mineral trapping, CO_2 can be safely, and virtually permanently, stored as nontoxic and stable carbonate minerals. In addition, because basaltic aquifers are widely distributed around the world, they can provide sufficient and easily accessible CO_2 storage space for sequestration of anthropogenic CO_2 . On land, huge areas of continental flood basalts are exposed, and most of the Earth's oceanic crust is basaltic. Consequently, basaltic aquifers are excellent candidates as CO_2 storage sites.

Because continental flood basalts are more easily accessible than deep-sea basalts, several experimental CO_2 storage research projects have already been conducted in flood basalt aquifers (Matter *et al.*, 2007; Gudbrandsson *et al.*, 2008; Schaef and McGrail, 2009), and a number of pilot injection projects are either underway or in the planning stages (Fig. 2); these include the Big Sky Carbon Sequestration Partnership (Columbia River Basalt Group: CRBG), the CarbFix Pilot Project (Icelandic basalts) and the Feasibility Study of Geologic Sequestration of CO_2 in Basalt Formations in India (Deccan Traps) (Litynski *et al.*, 2006; Matter *et al.*, 2009; Gislason *et al.*, 2010).

Several researchers have proposed that deep-sea basalts can also be used for CO_2 storage (Takahashi *et al.*, 2000; Goldberg *et al.*, 2008), pointing out that because deep-sea basalts are far more abundant than continental flood basalts, they can provide sufficient storage for huge volumes of anthropogenic CO_2 . Few studies, however, have investigated CO_2 storage in deep-sea basalt aquifers, in part because of the higher initial injection cost compared with continental basalt aquifers.

In this study, we assessed these two promising options for sequestration of anthropogenic CO_2 by comparing their geological and social-scientific advantages and disadvantages. Here, we focus on the post-injection period of CO_2 sequestration, especially potential storage capacity, leakage of injected CO_2 and the social-scientific impacts of CO_2 storage.

Region	Distribution area* (km ²)	Assumed net aquifer thickness (m)	Average porosity (%)	CO ₂ density (g/cm ³)	Age* (Ma)	Storage potential** (Gt CO ₂)	Mineral fxation potential (Gt CO ₂)
CRBG	164,000	10-100	15	0.4	16.6-15.3	98–984	792-7,921
Deccan Traps	500,000	10-100	15	0.4	66-65	300-3,000	2,732–27,320
Siberian Traps	1,500,000	10-100	15	0.4	251-250	900-9,000	7,690–76,900
Ethiopian Flood Basalts	500,000	10-100	15	0.4	31-29.5	300-3,000	2,605-26,050
Parana Flood Basalts	1,600,000	10-100	15	0.4	134-132	960-9,600	7,636-76,360
Icelandic Basalt	50,000	10-100	15	0.25	<26	19–188	297–2,965
Juan de Fuca	244,963	20-100	10	1	<15	490–2,450	2986-14929
East Pacific Rise	491,561	20-100	10	1	<15	983-4,916	6183-30913
Cocos Ridge	891,510	20-100	10	1	<15	1,783-8,915	11213-56064
Mid-Atlantic Ridge 60°N	52,734	20-100	10	1	<15	105-527	667-3336
Mid-Atlantic Ridge 40°N	139, 141	20-100	10	1	<15	287-1,391	1760-8802
Mid-Atlantic Ridge 0°	220,842	20-100	10	1	<15	442-2,208	2794-13971
Mid-Atlantic Ridge 40°S	3,778	20-100	10	1	<15	8–38	48–239
Southwest Indian Ridge 5°E	81,329	20-100	10	1	<15	163-813	962-4808
Southwest Indian Ridge 45°E	15,757	20-100	10	1	<15	32-158	184–931
Gulf of Aden	30,763	20-100	10	1	<15	62–308	364-1819
Southeast Indian Ridge	2,068,304	20-100	10	1	<15	4,137–20,683	24454-122271
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Table 1. Estimated CO_2 storage capacities and CO_2 mineral fixation potentials of deep-sea basalts and continental flood basalts

*Data are from Courtillot and Renne (2003) and Foulger (2006) for continental flood basalts and Goldberg and Slagle (2009) for deep-sea basalts. **Data are from Goldberg and Slagle (2009) for deep-sea basalts.

	CRBG	Deccan Traps	Siberian Traps	Ethiopian Flood Basalts	Parana Flood Basalts	Icelandic Basalt
SiO ₂ (wt.%)	51.34	50.37	49.89	48.06	51.68	48.6
TiO ₂	2.26	2.22	2.40	3.08	2.58	1.7
Al_2O_3	14.13	13.82	14.69	13.60	14.52	13.8
Fe ₂ O ₃ *	13.51		5.22	4.98		12.6
FeO*		12.65	8.02	7.66	12.86	
MnO	0.20		0.19	0.19	0.20	0.2
MgO	5.12	6.54	5.85	6.28	4.63	8.3
CaO	9.26	10.29	9.39	9.68	9.07	11.4
Na ₂ O	2.47	2.50	2.51	3.00	2.75	2.0
K ₂ O	1.06	0.63	1.51	1.11	1.26	0.3
P_2O_5	0.47	0.26	0.38	0.56	0.45	0.2
H ₂ O				1.50		
Total	99.81	99.27	100.04	99.70	100.01	98.4
LOI (%)						-0.70
References	(a)	(b)	(c)	(d)	(e)	(f)

Table 2. Average major-element compositions of continental flood basalts

 $Fe_2O_3^*$, FeO^* : CRBG and Icelandic Basalt, total iron as $Fe_2O_3^*$; Deccan Traps, total iron as FeO.

References: (a) Hooper (1988), (b) Mahoney (1988), (c) Zolotukhin and Al' mukhamedov (1988), (d) Mohr and Zanettin (1988), (e) Piccirillo et al. (1988), and (f) Gudbrandsson et al. (2008).

GEOLOGICAL AND GEOCHEMICAL ASSESSMENT

Continental flood basalts

Continental flood basalts originated from giant eruptions of basaltic lava over a short period of geological time (a few million years) are found in large igneous complexes (Haggerty, 1996). We studied the following six continental flood basalts as representative examples of suitable candidates for storage of CO_2 in basaltic aquifers: The CRBG in the northwestern United States, the Deccan Traps in northwestern India, the Siberian Traps in northern Russia, the Ethiopian Flood Basalts in Ethiopia and Yemen, the Parana Flood Basalts in southern Brazil and Icelandic Basalt in Iceland.

Flood basalts are typically formed by a series of eruptions that produce a massive complex composed of tens to hundreds of individual lava flows. Aquifer systems commonly develop in continental flood basalts because the uppermost section of each flow is composed of porous and permeable vesicular and brecciated basalts that serve as an efficient conduit for groundwater flow. In addition, because the sediment layers between individual basalt flows act as impermeable aguitards, the individual aquifer-aquitard systems are not connected. Thus, groundwater flow is dominantly horizontal. In general, the deeper a targeted formation is, the more secure the CO_2 storage is likely to be. Thus, targeted formations are typically at depths of at least 800 m, although the maximum target depth is about 1000 m because of the high cost of drilling injection wells. Temperature and pressure in a target formation are typically about 50°C and 8 to 10 MPa, respectively. Previously, it was believed that vertical groundwater movement within the aquifer systems of continental flood basalts is negligible, so that leakage of injected CO_2 to the surface would be unlikely (McGrail *et al.*, 2006; Matter *et al.*, 2009). However, the Columbia Basin Ground Water Management Area (GWMA, 2007) has reported natural vertical to subvertical groundwater movement through folds and faults within the CRBG aquifer systems. Therefore, detailed geological investigations of potential sequestration sites are needed to eliminate the possibility of CO_2 leakage from a target aquifer.

The estimated CO_2 storage potential of the CRBG aquifer system, the only one for which an estimate is available, is more 100 Gt CO₂ (McGrail et al., 2006). In the present study, we estimate the capacity of the Deccan Traps, Siberian Traps, Ethiopian Flood Basalts, Parana Flood Basalts and Icelandic Basalt, in addition to the CRBG, using assumptions similar to those of McGrail et al. (2006) (average porosity, 15%; net aquifer thickness from 10 m, one available interflow zone, to 100 m, 10 available interflow zones). McGrail et al. (2006) assumed a net aquifer thickness of 100 m (10 available interflows, each one 10 m thick), based on the research of Reidel et al. (2002). In this study, however, we assumed a net aquifer thickness from 10 m to 100 m. Because flood basalts consist of tens to hundreds of individual lava flows and the thickness of a typical target formation is about 200 m (depth from 800 to 1000 m), in the minimum case, it is possible for there to be only one available interflow zone and for the net thickness of the target aquifer to be only 10 m.

The storage capacity is calculated as follows:

$$C = A \cdot d \cdot n \cdot \rho_{\rm CO2} \tag{7}$$



Fig. 3. Conceptual diagrams of CO_2 storage in a deep-sea basalt aquifer and of the corresponding temperature and pressure conditions and seawater and CO_2 densities. Seafloor depth and the thickness of overlying sediments were assumed to be 3200 m and 300 m, respectively.

where *C* is the capacity of the continental flood basalt aquifer, *A* is the area of the target aquifer, *d* is the sum of thicknesses of the interflow zones of a multilayer aquifer, *n* is the porosity of the host rock and ρ_{CO2} is CO₂ density at the predicted temperature and pressure in the target aquifer.

In this calculation, the distribution area of each continental flood basalt was used as the aquifer area in the case of the CRBG, Deccan Traps, Siberian Traps, Ethiopian Flood Basalts and Parana Flood Basalts. In the case of the Icelandic Basalt only, the aquifer area was set to $50,000 \text{ km}^2$, which is about one-half the distribution area of the Icelandic Basalt (103,000 km²), to eliminate the active rift and its marginal zones, where there is a high possibility of leakage of injected CO₂ because of active volcanic eruptions and the development of fissures and cracks. For the CRBG, Deccan Traps, Siberian Traps, Ethiopian Flood Basalts and Parana Flood Basalts, we assumed a CO₂ density of 0.4 g/cm³ (i.e., 50°C and 10 MPa) based on the inferred target depth (800-1000 m) and temperature condition. We assumed the CO_2 density in the Icelandic Basalt to be 0.25 g/cm³ (60°C, 8 MPa) because of the steep geothermal gradient there (Alfredsson et al., 2008). The calculation results (Table 1) show that continental flood basalt aquifers have a large CO₂ storage potential (from 19–188 Gt CO_2 in the Icelandic Basalt to 960–9600 Gt CO_2 in the Parana Flood Basalts) and might be suitable for the sequestration of huge amounts of anthropogenic CO_2 .

We further estimated the mineral fixation potential of each continental flood basalt region (Table 1) under the assumption that all Ca, Mg and Fe in the host rock of aquifer would form carbonate minerals as a result of CO₂water-rock interactions (Eqs. (1)-(3)), and without taking into consideration other factors, such as changes in the physical characteristics of the host rock and groundwater chemistry. The major element compositions of the continental flood basalts used in the calculations are shown in Table 2. The mineral fixation potentials are about one order of magnitude higher than the estimated storage potentials (Table 1). Therefore, all of the CO₂ injected into the reservoir can be eventually fixed as carbonate minerals (mineral trapping). Note, however, that the mineral fixation potentials in the Deccan Traps, Siberian Traps and Parana Flood Basalts may be significantly smaller than the estimated values, because these basalts are much older than the others and, thus, the formation of secondary minerals, including carbonate minerals, by weathering has already proceeded to some extent (Table 1). For example, if 0.5 mol/kg carbon has already been fixed in carbonate minerals (about 50 g/kg of rock if the carbonate mineral is calcite), the maximum mineral trapping

	Juan de Fuca	East Pacific Rise	Mid-Atlantic Ridge	Mid-Indian Ocean Ridge
SiO ₂ (wt.%)	50.10	48.66	48.70	49.68
TiO,	1.59	1.68	0.86	1.57
Al_2O_3	14.63	15.18	16.29	15.44
Fe ₂ O ₃ *	12.15	11.59	10.32	10.80
MnO	0.21	0.20	0.17	0.19
MgO	7.39	9.04	9.30	8.27
CaO	12.00	11.08	11.80	10.80
Na ₂ O	2.50	2.46	2.35	3.27
K ₂ O	0.12	0.09	0.10	0.29
P_2O_5	0.16	0.15	0.07	0.15
Total	99.44	100.10	99.96	100.50
LOI (%)	_	0.87	0.51	0.45
References	(a)	(b)	(b)	(b)

Table 3. Average major-element compositions of deep-sea basalts (mid-ocean ridge basalts)

 $Fe_2O_3^*$, total iron as Fe_2O_3 .

References: (a) Smith et al. (1994) and (b) Sun et al. (1979).

Note: Chemical compositions of deep-sea basalts of the East Pacific Rise and Indian Ocean Ridge were also used for the Cocos Ridge and Gulf of Aden, respectively.

potential is lower than the estimates by about 9.6%, 10.2% and 11.0% in the Deccan Traps, Siberian Traps and Parana Flood Basalts, respectively.

Ocean-floor basalts

We also assessed the CO_2 storage potential of deepsea basalts around mid-ocean ridges. Although, CO2 storage has not yet been implemented in deep-sea basalt, CO_2 storage in sub-seafloor aquifers is already proceeding on a commercial scale. One example is the Sleipner project in Norway, which began in 1996 (IPCC, 2005). The Sleipner gas field is a natural gas field in the North Sea, about 250 km west of Stavanger, Norway. CO₂ from the produced gas is captured and stored in the Utsira Sand Formation, which is an offshore deep saline aquifer 800-1000 m below the seafloor. Since 1996, more than ten million tons of CO₂ have been injected into the aquifer. This practical example of CO₂ storage in the sub-seafloor aquifer clearly shows that no engineering problems exist to impede the implementation of CO₂ injection projects. In addition, CO_2 storage in a deep-sea basalt beneath the seafloor sediment may have an advantage from an engineering viewpoint because the management of formation pressures during drilling and injection is easier in (or beneath) unconsolidated sediments of the deep-sea environment than it is in continental geological formations (Schrag, 2009).

Suitable targets for CO_2 storage in oceanic crust are more than 3000 m below the sea surface, where at the seafloor pressure and temperature conditions CO_2 is stable as hydrate (Figs. 1(a) and 3). When thick sediments overlie young oceanic crust, temperatures above 60°C can be maintained within the crust (Sansone *et al.*, 1998). Under these conditions, the injected CO_2 is certain to

reach the supercritical phase. Because supercritical CO₂ is much less dense than the seawater in the sub-seafloor basalt aquifer (Fig. 1), the injected CO_2 will ascend through the oceanic crust if there are any faults or fissures. However, as the supercritical CO₂ rises to cooler levels, it will pass through the phase change point and enter the liquid phase (Figs. 1 and 3). As upward migration of the now liquid CO₂ continues, CO₂ is trapped at the stop point (where the density of the liquid CO₂ becomes equal to that of the surrounding pore water) (Figs. 1 and 3) by the gravitational trapping mechanism. Moreover, when the liquid CO_2 crosses the (water + c-h)/(water + liquid) boundary (where c-h is CO_2 clathrate hydrate) (Fig. 3), CO_2 hydrate is formed at the interface between the liquid CO_2 and the shallow pore water (Fig. 1). Because CO_2 hydrate is denser than seawater and less soluble than liquid CO₂ in water at temperatures below 2°C (Brewer et al., 1999), rapid dissolution and diffusion of CO₂ into shallow pore water or seawater is inhibited. In addition to the formation of liquid CO₂ and CO₂ hydrate, the thick layers of largely biogenic pelagic sediments overlying deep-sea basalts typically have extremely low permeabilities (nanodarcy order; Levine et al., 2007) and thus act as an impermeable caprock that further enhances the security of CO₂ storage. As a consequence, in deep-sea basalt aquifers, several impediments to leakage of injected CO_2 to the atmosphere (large potential for geochemical trapping, formation of liquid CO₂ and CO₂ hydrate, gravitational trapping, presence of an impermeable caprock, and dissolution in seawater) are commonly present. All these factors tend to make CO_2 storage in deep-sea basalt aquifer more secure.

Recently, House *et al.* (2006) proposed that CO_2 could be stored in deep-sea sediments overlying the deep-sea basalts. However, CO_2 injection into shallow sub-seafloor sediments may cause hydraulic fracturing, because of the extremely low permeability of pelagic sediments (Levine *et al.*, 2007). Such hydraulic fractures might reach the seafloor (Levine *et al.*, 2009) and allow the CO_2 to leak from the shallow sub-seafloor sediment aquifer.

Goldberg and Slagle (2009) estimated the storage capacity of deep-sea basalt by assuming a net aquifer thickness of 20-100 m, 10% rock porosity, and a CO₂ density of 1 g/cm³ (Table 1). They also assumed that all of the injected CO₂ would eventually be fixed as carbonate. They estimated the CO₂ storage capacity of the Juan de Fuca Ridge and Gulf of Aden between the Arabian Peninsula and the Horn of Africa, both of which are advantageously located near the continents, to be 491 to 2448 Gt CO₂ and 62 to 308 Gt CO₂, respectively. They also estimated the capacities of the East Pacific Rise, Cocos Ridge, Mid-Atlantic Ridge, Southwest Indian Ridge and Southeast Indian Ridge (Table 1). Overall, their results indicate that the CO₂ storage capacity of deep-sea basalt aquifers is at least comparable to and may even be much higher than that of continental flood basalt aquifers. In this study, we estimated the geochemical trapping potential of deep-sea basalt aquifers under assumptions similar to those used in the estimation of the storage capacity of continental flood basalts. The compositions of the deep-sea basalts used for our calculations are shown in Table 3. Our results show that, as in the case of the continental flood basalts, the mineral fixation potential of deep-sea basalts is much greater than their storage potential. Therefore, all of the CO_2 injected into a deep-sea basalt reservoir would also eventually be fixed as carbonate minerals.

SOCIAL-SCIENTIFIC ASSESSMENT

Even today, very few studies have dealt with the social-scientific implications of CO_2 storage in basaltic aquifers. As a result, the selection of potential storage sites has not taken into account societal needs. For large-scale implementation of CO_2 storage, social-scientific assessment is imperative and will be increasingly important in the future. Here, we discuss the socioeconomic conflicts that may arise from the use of basaltic aquifers for CO_2 storage.

From the social-scientific point of view, basaltic aquifers can be divided into two categories: freshwater and saline aquifers. In many regions of the world, freshwater aquifers are an important component of the water supply. They are especially important in landlocked arid to semiarid continental regions where many people depend on groundwater for their domestic and agricultural needs. However, water into which CO_2 has been injected is not available for agricultural or domestic use because CO_2 captured from thermal power plants is often contaminated with oxides of nitrogen and sulfur. In addition, harmful metals such as arsenic and lead present in the host rock may be mobilized by injected CO₂-aquifer water-host rock interactions (Zheng *et al.*, 2009). For instance, Pb²⁺ dissolved from minerals such as galena (PbS) forms a series of strong aqueous complexes with carbonate, such as Pb(CO₃)₂²⁻ and PbHCO₃⁺:

F

$$PbS + 2H^+ \rightarrow Pb^{2+} + H_2S(aq)$$
(8)

$$Pb^{2+} + 2CO_3^{2-} \rightarrow Pb(CO_3)_2^{2-}$$
 (9)

$$Pb^{2+} + HCO_3^{-} \to PbHCO_3^{+}.$$
 (10)

Hence, the solubility of Pb in the carbonated groundwater is very high, and the dissolved Pb can diffuse into and contaminate the surrounding groundwater (Wang and Jaffe, 2004). In a similar way, the groundwater may become contaminated by other harmful metals such as As and Zn. Moreover, the effect on groundwater quality of contamination with major elements such as Ca, Fe and Mn, whose concentrations can be increased by the injection of CO_2 , is also a consideration.

The groundwater in the CRBG, Icelandic Basalt and Deccan Traps has very low salinity (<0.05%) (Table 4); thus, these aquifers can be classified as freshwater aquifers. The aquifers in the CRBG and the Deccan Traps supply freshwater to surrounding regions. In the CRBG, several aquifers within a thick sequence of layered basaltic flows are the prime source of potable water and water for agriculture (GWMA, 2007). In the Deccan Traps, the basaltic aquifer is also an essential source of water for domestic and agricultural use (Kumar *et al.*, 2005). Therefore, a decline in groundwater quality or depletion of the groundwater resource in consequence of the use of these basalts for CO₂ storage would cause a critical decline in the economic value of the groundwater, at least in these two regions.

Moreover, groundwater depletion due to excessive pumping is already a problem in many regions of the world. Even in the CRBG, a test site for a pilot CO₂ injection project, groundwater extraction for irrigation, domestic water supply and industrial use has caused water levels to decline by more than 50 m in several areas (Reilly et al., 2008). Similar groundwater depletion problems have been reported in northern India, including part of the Deccan Traps. According to Rodell et al. (2009), groundwater is being greatly depleted in the northwestern Indian states of Rajasthan, Punjab and Haryana. Because the population of India is growing dramatically, it is very likely that groundwater depletion problems will continue to increase. Even if the target formations for CO_2 storage are generally deeper than the formations used for water supply, groundwater is likely to become polluted by the injection of CO_2 (and its associated pollutants) into aquifers in continental flood basalts as a result of vertical flows of the injected CO_2 and polluted groundwater. Consequently, large-scale CO_2 storage in freshwater aquifers in continental flood basalts would inevitably elicit societal objections.

Different from freshwater aquifers, groundwater depletion is not a problem in saline target aquifers because they have no economic value; thus, there are no socialscientific problems raised by the implementation of largescale CO₂ storage projects. The total CO₂ storage potential of continental flood basalt aquifers decreases substantially, however, if only saline aquifers can be targeted. In contrast to CO₂ storage in continental flood basalt aquifers, such problems do not arise in the case of CO₂ storage in deep-sea basalt aquifers, because all deep-sea basalt aquifers are saline and the seawater circulating in the aquifers has no economic value. Our social-scientific assessment thus leads us to conclude that the CO₂ storage potential of deep-sea basalt aquifers for sequestration of anthropogenic CO_2 is much higher than that of continental basalt aquifers.

SELECTION OF BASALTIC AQUIFERS FOR CO2 STORAGE

Here, we compare the suitability for CO₂ storage in continental flood basalt and deep-sea basalt aquifers in light of our geological and geochemical and socialscientific assessments. From geological and geochemical perspectives, CO₂ storage potential is one of the most important considerations in evaluating the suitability of different storage options. Both the CO₂ storage and mineral fixation potentials of deep-sea basalt aquifers are at least equal to, if not much greater than, those of continental flood basalt aquifers. Aquifer temperature is another important consideration, because it controls the rates of the chemical reactions for geochemical trapping of CO₂. Predicted temperatures in deep-sea basalt aquifers (above 60°C) are about the same or slightly higher than those in continental flood basalt aquifers (50°C). In addition, there is little difference in the major element compositions between continental flood and deep-sea basalts, despite their different formation processes. The main difference is that pressure in deep-sea basalt aquifers (30 MPa) is about three times that in continental flood basalt aquifers (8 to 10 MPa), but the effect of hydrostatic pressure on water-rock interactions is negligible. Although the rock dissolution rate is also influenced by factors other than temperature, pressure, groundwater chemistry and host rock property (e.g., crystallinity, rock alteration and fracturing), the geochemical trapping rate is unlikely to differ greatly between continental flood basalt and deepsea basalt aquifers. From the viewpoint of CO₂ storage security, deep-sea basalt aquifers are more secure against

	Columbi	a River Basa	lt Group (CRBG) ^a	Ice	landic Basalt ^b			Deccan Traps ^c	
	DC-06	DB-11	Jw-1	Pr-3	Langjokull ^d	Laxa in Kjos	HN-1	Sagar Univ.	Mehidpur, Ujjain Dt.	Titarpani Sagar Dt.
Hq	9.92	7.94	7.86	8.06	5.30	7.69	8.58	7.2	7.1	7.2
Na (mmol/kg)	11.6	1.37	1.43	2.49	3.10	0.23	1.57	1.7	3.7	0.8
K (mmol/kg)	0.22	0.27	0.25	0.28	0.45	0.01	0.03	0.018	0.038	0.013
Ca (mmol/kg)	0.06	0.38	0.46	0.52	0.15	0.09	0.18	1.3	1.6	2.1
Mg (mmol/kg)	0.01	0.30	0.83	0.34	0.35	0.07	0.33	2.4	3.8	1.1
H_4SiO_4 (mmol/kg)	1.79	0.96	1.02	0.80	0.00	0.15	2.11	1.2	1.0	1.3
Cl (mmol/kg)	4.57	0.12	0.17	0.28	3.15	0.26	0.25	0.93	4.5	0.37
SO_4 (mmol/kg)	1.48	<0.0005	0.22	0.00				0.21	0.74	0.016
^a Data from Stevens . ^b Data from Gysi and ^c Data from Lunkad . ^d Units are µmol/kg.	and Mckin I Stefansso and Rayma	ley (1995). na (2008). nhashay (195	78).							

Table 4. Groundwater chemistry in the Columbia River Basalt Group, Icelandic Basalt and Deccan Traps continental flood basalts, where pilot CO.

leakage of CO_2 to the atmosphere by virtue of the presence of multiple barriers: overlying thick, low-permeability marine sediments acting as a caprock, gravitational trapping of CO_2 in the aquifer, the formation of CO_2 hydrate on and just below the seafloor and the dissolution of CO_2 into overlying seawater.

From a social-scientific perspective, some continental flood basalts are freshwater aquifers that are an important groundwater source for domestic and agricultural needs. However, water contaminated by injected CO_2 is not available for agricultural and domestic use. Because CO_2 storage in continental flood basalt aquifers could cause depletion of precious freshwater resources, largescale CO_2 storage in basaltic aquifers in many continental flood basalt regions is problematic. In striking contrast, aquifers in deep-sea basalts present no comparable problems because the saline aquifer waters, of seawater origin, have no economic value.

Our geological, geochemical and social-scientific analyses show that deep-sea basalt aquifers are a better option for CO₂ storage than continental flood basalt aquifers, even though access to deep-sea basalts may be more difficult and costly. We should bear in mind that CO₂ storage capacity is an important parameter in economic assessment, and serious conflict with freshwater resources can critically decrease the storage potential of continental flood basalt aquifers, thus offsetting the economic advantage of this option, whereas the large storage capacity of deep-sea basalts improves the economic assessment. In either case, further comprehensive investigations and detailed estimation of CO₂ storage capacity are needed for more realistic economic assessment of CO₂ injection sites. In addition, the assessments must be supported by laboratory simulations and pilot experiments, especially in the case of deep-sea basalts.

CONCLUSIONS

On the basis of our geological, geochemical and social-scientific assessments of continental flood basalt and deep-sea basalt aquifers as potential CO_2 storage sites, we arrived at the following conclusions:

(i) From a geological and geochemical perspective, the CO_2 storage potential of deep-sea basalt aquifers is at least equal to and may even be much greater than that of continental flood basalt aquifers. Moreover, CO_2 storage in deep-sea basalts may be more secure, because of the presence of multiple barriers against CO_2 leakage to the atmosphere, including a thick caprock of impermeable marine sediments, gravitational trapping of CO_2 , formation of CO_2 hydrate and dissolution of CO_2 in the seawater.

(ii) From a social-scientific perspective, implementation of large-scale CO_2 storage in continental flood basalts containing freshwater aquifers can cause contamination of an already diminishing prime freshwater resource. Large-scale CO_2 storage in such aquifers would, therefore, inevitably conflict with other societal needs. As a result, implementation of CO_2 storage in basaltic aquifers in many continental flood basalt regions would be problematic. In contrast, such problems do no arise from the use of deep-sea basalt aquifers for CO_2 storage because deep-sea basalt aquifers contain only unusable saline water.

(iii) Therefore, deep-sea basalt aquifers are a better option for large-scale implementation of CO_2 storage than continental flood basalt aquifers.

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REFERENCES

- Alfredsson, H. A., Hardarson, B. S., Franzson, H. and Gislason, S. R. (2008) CO₂ sequestration in basaltic rock at the Hellisheidi site in SW Iceland: stratigraphy and chemical composition of the rocks at the injection site. *Mineral. Mag.* 72, 1–5.
- Bachu, S. (2002) Sequestration of CO_2 in geological media in response to climate change: road map for site selection using the transform of the geological space into the CO_2 phase space. *Energy Conv. Manag.* **43**, 87–102.
- Bachu, S. (2003) Screening and ranking of sedimentary basins for sequestration of CO_2 in geological media in response to climate change. *Environ. Geol.* **44**, 277–289.
- Bachu, S., Gunter, W. D. and Perkins, E. H. (1994) Aquifer disposal of CO₂—Hydrodynamic and mineral trapping. *Energy Conv. Manag.* 35, 269–279.
- Brewer, P. G., Friederich, C., Peltzer, E. T. and Orr, F. M. (1999) Direct experiments on the ocean disposal of fossil fuel CO₂. *Science* **284**, 943–945.
- Courtillot, V. E. and Renne, P. R. (2003) On the ages of flood basalt events. *C. R. Geosci.* **335**, 113–140.
- Diamond, L. W. and Akinfiev, N. N. (2003) Solubility of CO₂ in water from -1.5 to 100 degrees C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. *Fluid Phase Equilib.* **208**, 265–290.
- Foulger, G. R. (2006) Older crust underlies Iceland. *Geophys. J. Int.* **165**, 672–676.
- Gislason, S. R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E. H., Gunnlaugsson, E., Sigurdardottir, H., Sigfusson, B., Broecker, W. S., Matter, J. M., Stute, M., Axelsson, G. and Fridriksson, T. (2010) Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. Int. J. Greenh. Gas Control 4, 537–545.
- Goldberg, D. and Slagle, A. L. (2009) A global assessment of deep-sea basalt sites for carbon sequestration. *Energy Procedia* 1, 3675–3682.
- Goldberg, D. S., Takahashi, T. and Slagle, A. L. (2008) Carbon

dioxide sequestration in deep-sea basalt. *Proc. Natl. Acad. Sci. USA* **105**, 9920–9925.

- Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S. R. and Oelkers, E. H. (2008) Dissolution rates of crystalline basalt at pH 4 and 10 and 25–75°C. *Mineral. Mag.* **72**, 155–158.
- GWMA (Columbia Basin Ground Water Management Area) (2007) Geologic Framework of Selected Sediment and Columbia River Basalt Units in the Columbia Basin Ground Water Management Area of Adams, Franklin, Grant, and Lincoln Counties, Washington, D.C., 78 pp.
- Gysi, A. P. and Stefansson, A. (2008) Numerical modelling of CO₂-water-basalt interaction. *Mineral. Mag.* 72, 55–59.
- Haggerty, B. M. (1996) Episodes of flood-basalt volcanism defined by ⁴⁰Ar/³⁹Ar age distributions: Correlation with mass extinctions? J. Undergrad. Sci. **3**, 155–164.
- Hooper, P. R. (1988) The Columbia River Basalt. Continental Flood Basalts (Petrology and Structural Geology) (Macdougal, J. D., ed.), 1–33, Kluwer Academic Publ.
- House, K. Z., Schrag, D. P., Harvey, C. F. and Lackner, K. S. (2006) Permanent carbon dioxide storage in deep-sea sediments. *Proc. Natl. Acad. Sci. USA* 103, 12291–12295.
- IPCC (2005) Carbon Dioxide Capture and Storage IPCC Special Reports. Cambridge Univ. Press, 431 pp.
- Kharaka, Y. K., Cole, D. R., Thordsen, J. J., Kakouros, E. and Nance, H. S. (2006) Gas-water-rock interactions in sedimentary basins: CO₂ sequestration in the Frio Formation, Texas, USA. J. Geochem. Explor. 89, 183–186.
- Kongsjorden, H., Karstad, O. and Torp, T. A. (1997) Saline aquifer storage of carbon dioxide in the Sleipner project. *Waste Manag.* **17**, 303–308.
- Kumar, R., Singh, R. D. and Sharma, K. D. (2005) Water resources of India. *Curr. Sci.* 89, 794–811.
- Levine, J. S., Matter, J. M., Goldberg, D., Cook, A. and Lackner, K. S. (2007) Gravitational trapping of carbon dioxide in deep sea sediments: Permeability, buoyancy, and geomechanical analysis. *Geophys. Res. Lett.* 34, L24703.
- Levine, J. S., Matter, J. M., Goldberg, D. and Lackner, K. S. (2009) Gravitational trapping of carbon dioxide in deep ocean sediments: hydraulic fracturing and mechanical stability. *Energy Procedia* 1, 3647–3654.
- Litynski, J. T., Klara, S. M., McIlvried, H. G. and Srivastava, R. D. (2006) The United States Department of Energy's Regional Carbon Sequestration Partnerships Program: A collaborative approach to carbon management. *Environ. Int.* 32, 128–144.
- Lunkad, S. K. and Raymahashay, B. C. (1978) Ground water quality in weathered Deccan Basalt of Malwa Plateau, India. J. Eng. Geol. Hydrogeol. 11, 273–277.
- Mahoney, J. J. (1988) Deccan traps. *Continental Flood Basalts* (*Petrology and Structural Geology*) (Macdougal, J. D., ed)., 151–194, Kluwer Academic Publ.
- Matter, J. M. and Kelemen, P. B. (2009) Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nature Geoscience* **12**, 837–841.
- Matter, J. M., Takahashi, T. and Goldberg, D. (2007) Experimental evaluation of in situ CO_2 -water-rock reactions during CO_2 injection in basaltic rocks: Implications for geological CO_2 sequestration. *Geochem. Geophys. Geosyst.* **8**, Q02001.

- Matter, J. M., Broecker, W. S., Stute, M., Gislason, S. R., Oelkers, E. H., Stefánsson, A., Wolff-Boenisch, D., Gunnlaugsson, E., Axelsson, G. and Björnsson, G. (2009) Permanent carbon dioxide storage into basalt: The CarbFix Pilot Project, Iceland. *Energy Procedia* 1, 3641–3646.
- McGrail, B. P., Schaef, H. T., Ho, A. M., Chien, Y. J., Dooley, J. J. and Davidson, C. L. (2006) Potential for carbon dioxide sequestration in flood basalts. J. Geophys. Res. 111, B12201.
- Mohr, P. and Zanettin, B. (1988) The Ethiopian Flood Basalt Province. *Continental Flood Basalts (Petrology and Structural Geology)* (Macdougal, J. D., ed.), 63–110, Kluwer Academic Publ.
- Piccirillo, E. M., Melfi, A. J., Comin-Chiaramonti, P., Bellieni,
 G., Ernesto, M., Marques, L. S., Nardy, A. J. R., Pacca, I.
 G., Roisenberg, A. and Stolfa, D. (1988) Continental flood
 volcanism from the Parana Basin (Brazil). *Continental Flood Basalts (Petrology and Structural Geology)* (Macdougal, J. D., ed.), 195–238, Kluwer Academic Publ.
- Reidel, S. P., Johnson, V. G. and Spane, F. A. (2002) Natural gas storage in basalt aquifers of the Columbia Basin, Pacific Northwest USA: A guide to site characterization. Rep. PNNL-13962, Pac. Northwest Natl. Lab., Richland, Wash.
- Reilly, T. E., Dennehy, K. F., Alley, W. M. and Cunningham, W. L. (2008) Ground-Water Availability in the United States. U.S. Geological Survey, Circular 1323, 70 pp.
- Rodell, M., Velicogna, I. and Famiglietti, J. S. (2009) Satellitebased estimates of groundwater depletion in India. *Nature* 460, 999–1002.
- Sansone, F. J., Mottl, M. J., Olson, E. J., Wheat, C. G. and Lilley, M. D. (1998) CO₂-depleted fluids from mid-ocean ridgeflank hydrothermal springs. *Geochim. Cosmochim. Acta* 62, 2247–2252.
- Schaef, H. T. and McGrail, B. P. (2009) Dissolution of Columbia River Basalt under mildly acidic conditions as a function of temperature: Experimental results relevant to the geological sequestration of carbon dioxide. *Appl. Geochem.* 24, 980–987.
- Schrag, D. P. (2009) Storage of carbon dioxide in offshore sediments. *Science* 325, 1658–1659.
- Smith, M. C., Perfit, M. R. and Jonasson, I. R. (1994), Petrology and geochemistry of basalts from the southern Juan de Fuca Ridge: controls on the spatial and temporal evolution of mid-ocean ridge basalt. J. Geophys. Res. 99, 4787–4812.
- Stevens, T. O. and Mckinley, J. P. (1995) Lithoautotrophic microbial ecosystems in deep basalt aquifers. Science 270, 450–454.
- Suekane, T., Nobuso, T., Hirai, S. and Kiyota, M. (2008) Geological storage of carbon dioxide by residual gas and solubility trapping. *Int. J. Greenh. Gas Control* 2, 58–64.
- Sun, S. S., Nesbitt, R. W. and Sharaskin, A. Y. (1979) Geochemical characteristics of mid-ocean ridge basalts. *Earth Planet. Sci. Lett.* 44, 119–138.
- Takahashi, T., Goldberg, D. and Mutter, J. C. (2000) Secure, long-term sequestration of CO₂ in deep saline aquifers associated with oceanic and continental basaltic rocks. *Proc. SRI Int. Symp., Deep Sea & CO₂ (The Ship Research Institute, Mitaka)*, pp. 4-1-1–4-1-7.
- UNESCO (1983) Algorithms for computation of fundamental

properties of seawater. UNESCO Technical Papers in Marine Science 44, 53 pp.

Wang, S. and Jaffe, P. R. (2004) Dissolution of a mineral phase in potable aquifers due to CO₂ releases from deep formations; effect of dissolution kinetics. *Energy Conv. Manag.* 45, 2833–2848.

Zheng, L. G., Apps, J. A., Zhang, Y. Q., Xu, T. F. and Birkholzer,

J. T. (2009) On mobilization of lead and arsenic in ground-water in response to CO_2 leakage from deep geological storage. *Chem. Geol.* **268**, 281–297.

Zolotukhin, V. V. and Al'mukhamedov, A. I. (1988) Traps of the Siberian Platform. *Continental Flood Basalts (Petrology and Structural Geology)* (Macdougal, J. D., ed.), 273– 310, Kluwer Academic Publ.