CO₂ Mobility in Natural Reservoirs Beneath the Colorado Plateau and Southern Rocky Mountains: An Example from the Springerville-St. Johns Field, Arizona and New Mexico

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Abstract

The Springerville-St. Johns CO₂ field in eastern Arizona and western New Mexico is one of more than a dozen gas fields developed within the Colorado Plateau and Southern Rocky Mountain region. The reservoir is associated with spectacular travertine deposits that cover an area of about 250 km². Pressure measurements from deep exploration wells indicate that springs in the travertine area could be fed by lateral outflow of water from the region of the CO₂ field. Groundwater in the immediate vicinity of the gas field is enriched in HCO₃ and displays the highest degree of dolomite supersaturation. Interactions between the basin fluids and the clastic sediments that host the CO₂ reservoir resulted in the dissolution of carbonate cements and detrital feldspars and the formation of kaolinite and rare dawsonite. Geochemical simulations indicate that kaolinite will become stable at a CO₂ fugacity of <1 bar but that a fugacity of 20 bar is required to stabilize dawsonite. The limited occurrence of dawsonite may reflect the presence of local anhydrite-rich seals that allowed high CO₂ fugacities to develop. Taken together, the results of these mineralogic and geochemical investigations demonstrate that the Springerville-St Johns CO₂ field represents a natural analogue for evaluating the potential effects of CO₂ leakage from subsurface reservoirs with imperfect seals and the effects of mineral sequestration.

Keywords: CO₂ field, Springerville-St. Johns, dawsonite, water chemistry

Introduction

Increasing global interest in geologic sequestration of CO_2 has raised important questions about its longterm fate. Geochemical models suggest that substantial amounts of CO_2 injected into deep reservoirs can be removed through fluid-fluid and fluid-mineral reactions, particularly those that lead to the formation of Ca, Fe and Mg carbonates (e.g. Gunter et al., 1993; Bachu et al., 1994, Perkins and Gunter, 1996; Xu et al. 2001). Because CO_2 -charged ground waters are chemically reactive, other minerals, including zeolites, kaolinite and quartz can be expected to form through reactions involving HCO₃ and the host rocks. Such reactions, for example, are typical of the marginal parts of modern geothermal systems, which are characterized by argillic alteration and calcite (Hedenquist and Stewart, 1985). However, autoclave experiments designed to test predictions of the geochemical models have been hampered by the slow kinetics of the mineral reactions (Gunter et al., 1996, 1997; Pearce et al., 1996).

Few studies of natural CO₂ reservoirs are currently available to determine the efficiency of mineral sequestration and the effects of fluid-mineral reactions. Pearce et al. (1996) suggested that the influx of CO₂-rich groundwater into the Bravo Dome of New Mexico resulted in the dissolution of anhydrite, dolomite and plagioclase and the formation of kaolinite and zeolites. On the other hand, ongoing investigations of the productive White Rim Sandstone in the Gordon Creek field, Utah, showed no clear evidence of interactions between CO₂-rich fluids and the host rocks (J. Moore, unpub. data).

In this paper, the results of geochemical and hydrologic investigations conducted on the Springerville-St. Johns CO_2 field in eastern Arizona and western New Mexico are described. It is one of more than a dozen generally similar CO_2 reservoirs developed in domed Mesozoic and Paleozoic sedimentary rocks of the Colorado Plateau and Southern Rocky Mountain region of the western U.S. (Fig. 1; Allis et al., 2001). Within these reservoirs siliciclastic rocks, and to a lesser extent carbonates, serve as the primary aquifers, whereas anhydrite beds and mudstones act as local seals. The Ridgeway Arizona Oil Corp. is presently developing the Springerville-St. Johns field for CO_2 and He.

The Springerville-St. Johns field is significant for three reasons. First, spectacular travertine deposits, which we suggest record the effects of long term CO_2 leakage from the reservoir, are present. Leakage of CO_2 and other gases to the atmosphere is an important consideration in any sequestration project. Second, core from the CO_2 reservoir is available for petrologic studies. These samples provide direct mineralogic evidence of interactions between the CO_2 -charged fluids and the host rocks. Finally, pressure data from deep wells and chemical analyses of well and spring waters are available. These data provide insight into the fluid flow paths and the hydrologic connections between the deep and shallow fluids.

Geologic Setting of the Springerville-St. Johns Area

The Springerville-St. Johns CO₂ field covers approximately 1813 km² (Rauzi, 1999) on the southeastern edge of the Colorado Plateau, east of the Pio-Pleistocene Springerville volcanic field (Sirrine, 1951; Crumpler et al., 1994). K-Ar ages of the basaltic rocks that make up this field range from ~0.3 to 3 Ma. (Condit et al., 1994). The CO₂ field and the travertine deposits lie adjacent to the Little Colorado River (Fig. 2). The gas reservoir is developed in Permian rocks that define a broad, northwest-trending asymmetrical anticline with steeper dips on the faulted southwest flank of the structure. This fault zone is thought to be controlled by Precambrian structure that affects the underlying granitic rocks.

The producing zones in the St. Johns-Springerville field occur primarily in the Fort Apache Limestone Member, Big A Butte Member, and Amos Wash Member of the Supai Formation (Fig. 3; Rauzi, 1999). The Fort Apache Limestone Member consists of red siltstones capped by anhydrite and underlain by dolomite. The Big A Butte Member is composed of 5 anhydrite beds within a sequence of red siltstones and minor dolomite. The Amos Wash Member is heterogeneous, consisting of red mudstones, siltstones, and very fine-grained sandstones. At the base of the unit, it contains lenses of conglomerate with fragments of the underlying Precambrian granitic rocks. These lenses are interpreted as channel fillings. The granitic rocks are highly altered and in one well contain abundant secondary dolomite. Gas has been reported from the conglomerates and it is likely that CO₂-charged fluids have circulated through the fractured granite. However, a relationship between the alteration of the granite and these fluids has not yet been established.

Drill stem and initial flow tests indicate that the wells can produce up to approximately 2000 Mcf per day (Rauzi, 1999). Analyses of the gas from the 1 Plateau Cattle well and the 3-1 State well yielded 90% CO_2 , 6-10% N_2 , and 0.5 to 0.8% He, and 0.1% each of CH_4 and Ar, although some wells are reported to produce gas with higher CO_2 contents. The 1 Plateau Cattle well produced 640 Mcf of gas and 436 barrels of water per day. The CO_2 -charged waters are chemically aggressive due to their acidity and the 1 Plateau Cattle well had to be replaced because of corrosion to the steel casing.

The Ridgeway Arizona Oil Corp. cut 210 m of conventional core in 3 wells drilled in Arizona and 233m of core in 5 wells drilled in New Mexico. In addition, sidewall cores were taken. Conventional and sidewall core samples from 5 of the Arizona wells (9-21 State, 10-22 State, 10-26 State, 11-21 State, and 22-1X State; refer to Fig. 2) that include samples of the Precambrian granite were collected for study. All but 10-26 State produced dry gas or CO₂-charged waters in drill-stem or flow tests. The 10-22 State well has been producing CO₂ for a liquid CO₂ plant since July 2002.

Travertine Deposits

The Springerville-St Johns area contains one the greatest concentrations of travertine spring deposits in the U.S. These carbonate deposits cover an area of approximately 250 km² primarily south and east of St. Johns (Sirrine, 1951). They are particularly prevalent adjacent to a 10 km length of the Little Colorado River between Lyman Lake and Salado Springs (Fig. 2), where numerous springs and seeps occur today. None of the springs had temperatures greater than 10°C above ambient.

Many of the individual deposits are unusually large and symmetric (Fig. 4; Crumpler et al., 1994). Travertine sheets up to 6.4 by 3.2 km in extent and circular domes up to 610 m in diameter suggest a long history of spring discharge (Sirrine, 1951). The domes typically contain large central chambers that mark

the locations of the spring vents. The sheets and domes occur adjacent to seepage areas as well as on terraces up to nearly 60 m above the valley floor. The height of the cones is often difficult to determine because the travertine frequently caps raised terraces of sedimentary rocks (typically red Moenkopi Formation). Based on assumptions about the elevation of the underlying sedimentary platform, most of the domes have travertine thicknesses ranging in height from less than 3 to about 60 m.

The size of the travertine deposits presumably points to a long history of continued outflow with a nearly constant head from the same vent positions. The age of the travertine deposits, however, is uncertain. Sirrine (1954) suggested that deposition of the deposits began in the late Pleistocene because they postdate the basaltic volcanism and are locally interbedded with late Pleistocene Richville Formation gravels. No older deposits are known. Compared to the extent of past activity implied by the large fossil deposits, travertine deposition appears to be relatively insignificant today. Furthermore, none of the dome-like features are currently forming.

Springs can change their location and elevation over time as erosion occurs and lowers the base level controlling the local groundwater hydrology. In the Crystal Geysers area of central Utah, extinct travertine deposits are preserved several tens of meters above the active springs located adjacent to the Green River (Doelling, 1994). Erosion rates in tributaries of the Colorado River in central and southern Utah range from $\sim 20-40$ cm/1000 years (Biek et al., 2000; Baer and Rigby, 1978; Doelling, 1994). Based on these rates, travertine deposition at Crystal Geysers could have begun 10^4-10^5 years ago. Similar erosion rates are probable in the arid Little Colorado River area of Arizona. If it is assumed that the differences in the elevations of the travertine deposits in the Springerville-St. Johns area is due to erosion and a change in the base level of the Little Colorado River, then it is possible that some of the travertine could have been deposited as much as 10^5 years ago. However, the apparent lack of extensive erosion of some of the larger, higher elevation deposits suggests that factors other than a declining base level may have influenced the drop in activity. These factors could include a combination of climactic and hydrologic changes and a decrease in the CO₂ partial pressure at depth. In this case, the travertine deposits could be much younger than indicated by the erosion rates.

Hydrology of the Springerville-St. Johns Travertine Area

All flowing features in the travertine area appear to be less than 3 m above the elevation of the Little Colorado River, suggesting that the river is the primary control on the outflows. Some of the pools had no obvious overflow and presumably were leaking below the ground surface. The greatest outflows appeared to be in a swampy area immediately below the Lyman dam (estimated to be about 10 l/s), and in the swampy area of Salado Springs (about 15 l/s).

Figure 5 shows the pressure-elevation trends for the St. Johns-Springerville area. Two trends are apparent. The travertine- CO_2 field forms one obvious aquifer with a pressure intercept close to 1830 m above sea level (asl). The Tucson Electric Power Co. groundwater wells have been plotted collectively by showing an average head (zero pressure) at 1830 m asl although actual water levels rise to over 1890 m asl on the east side of the Salado Springs fault zone (unpublished Tucson Electric Power Co. data). The scatter in pressures from the Ridgeway Arizona Oil Corp. wells is consistent with localized zones of CO_2 causing slightly higher pressures at the top of the gas zones, but the overall near-hydrostatic trend shows the system is water-dominated. This pressure trend explains how the springs and pools adjacent to the Little Colorado River area could be fed by lateral outflow of water from the region of the CO_2 field.

Within ~8 to16 km west of Salado Springs, the pressure trend is significantly different, and indicates a laterally extensive aquifer system that has a pressure intercept at about 1525 m asl. This elevation is similar to that of the Little Colorado River about 16 km west of Holbrook. It is possible that the Kaibab-Glorieta aquifer is in pressure equilibrium with surface water in that location. The cross-section in Figure 6 illustrates this lateral change in potentiometric head and compares it to the gross structural changes in some of the main sedimentary units. The transition between the two pressure trends is poorly controlled and perched groundwater aquifers may overlie the deep hydrologic units identified here.

Fluid Chemistry

The compositions of waters from the Springerville - St. Johns region were studied to evaluate their relationships to the CO_2 field and to assess the ability of the reservoir rocks to sequester CO_2 through naturally occurring water-rock interactions. The geochemical data were taken from compilations of groundwaters by Mann and Nemecek (1983), geothermal waters by Witcher (1995), unpublished analyses of well waters provided by Tucson Electric Power Co and Ridgeway Arizona Oil Corp. and analyses of spring and shallow well waters collected by the authors during the spring of 2002. Although the number of analyzed chemical species varied, all of the analyses contained data on the dominant groundwater ions Na, K, Ca, Mg, HCO₃, SO₄ and Cl. The quality of each analysis, which depends on the purpose of the sampling, was found to range from poor to good. The analytical quality was evaluated by calculating the charge balance. Poor quality analyses can have an adverse effect on thermodynamic modeling efforts; however, even poor quality analyses can be used to track water types.

The locations of the water samples utilized in this study are shown in Figure 7. The waters range continuously in chemical character from Ca-Mg HCO₃ to Ca-Mg Cl-SO₄ (Fig. 8). The distribution of water types is illustrated in Figure 9. Although the waters are high in HCO₃, SO₄ and Cl, these constituents are not necessarily coupled. Relationships shown on the piper plot in Figure 8 indicate the samples are a mixture of Ca-Mg HCO₃ and Na SO₄-Cl waters. The SO₄/Cl and Ca/Mg components display reasonably constant ratios, while HCO₃ and Na proportions of the anions and cations respectively range from less than 40% to nearly 100%. This suggests that the concentrations of SO₄, Ca, and Mg are determined by a combination of source rock abundances and fluid-mineral equilibria, while acidification and neutralization caused by the addition of CO₂ are responsible for the variations in HCO₃ and Na (e.g. Mahon et al., 1980). Na-K HCO3, Na-K HCO3-SO4, and Ca Cl water types dominate in the immediate vicinity of the CO₂ field.

The hydrologic data suggest a possible connection between the basin waters and the waters that discharge from Salado Springs. Water from the Ridgeway Arizona Oil Corp. well 11-21 State is Na-K HCO₃-SO₄ in character (Table 1). In contrast, waters from the Tucson Electric Power Co. wells and Salado Springs are Na Cl in character, although the Salado Springs water is also enriched in HCO₃. It can be postulated that the Salado Springs water is a mixture of waters encountered in the CO_2 field wells and the power plant wells. Possible mixing relationships were examined by considering ratios of the conservative components B and Cl. Although B/Cl ratios are relatively constant proportions of reactive components such as Ca, Mg and SO₄ differ among the waters. Thus, the compositions of the spring and deep waters may reflect the effects of multicomponent mixing and water-rock interactions.

Mineralogy of the CO₂ Reservoir Rocks

Mineral assemblages and textures in core samples representative of the Permian Supai Formation encountered between depths of 420 and 825 m and the underlying Precambrian granite were examined in detail. Approximately 100 samples were studied petrographically in thin section. Mineral identifications were supported by X-ray diffraction analyses of bulk rock and clay (<5micrometer) separates of 41 samples. A scanning electron microscope equipped with an EDX analyzer provided additional key textural data and qualitative chemical analyses of mineral phases. The core samples of the Supai Formation consisted dominantly of red, fine-grained siltstones intercalated with minor sandstone, anhydrite, limestone and dolomite beds.

Despite the relatively large number of samples that were examined, only those from depths between 462 and 472 m in well 22-1X yielded clear evidence of reactions that could be related to interactions with CO_2 -rich fluids. These samples are characterized by the dissolution of authigenic cements and detrital feldspar grains and by the formation of dawsonite (NaAlCO₃(OH)₂) and kaolinite. Well 22-1X produced 1894 Mcf per day of gas from depths of 463-495 m. Other cored intervals in this well were not tested. This interval is significant because it is the only interval sampled that produced CO_2 gas. Cored intervals in other wells were either non productive or produced water containing various proportions of gas.

The presence of dawsonite is significant because themochemical calculations suggest that it may be an important mineral sink for CO₂ in deep continental aquifers (Knauss et al., 2001; Johnson et al., 2002; White et al., 2002; Xu et al., 2002; Zerai et al., 2002; Boram et al., 2003). These models indicate that dawsonite can form relatively rapidly, particularly when compared to other carbonate minerals Although dawsonite is a relatively uncommon authigenic mineral, it does occur in a variety of geologic environments. Dawsonite has been observed in clastic and volcaniclastic sedimentary rocks and coals, as a weathering product of soils and as a hydrothermal mineral associated with intrusive and volcanic rocks. Baker et al. (1995) have provided particularly detailed descriptions of dawsonite occurrences in the Bowen-Gunnedah-Sydney basin system, Australia where it is widely distributed in Permo-Triassic marine and nonmarine rocks as a cement, replacement of framework grains and pore-filling mineral. Although they did not consider growth of dawsonite to have occurred under present-day conditions, the lack of deformation of individual dawsonite fibers led Baker et al. (1995) to conclude that dawsonite was deposited after deposition of other authigenic minerals and compaction of the sediments. At Olduvai Gorge in Africa, dawsonite is associated with zeolites and sodium carbonate minerals in arid alkaline soils (Hay, 1963). In the United States, dawsonite has previously only been identified in saline, alkaline lacustrine basins, such as in the Green River Formation of Eocene Lake Uinta (Hay, 1964; Smith and Milton, 1966; Mason, 1983; Daub et al., 1985). In the following sections, we describe the geologic occurrence of dawsonite at Springerville-St. Johns and then present the results of thermochemical models that help explain its origin.

Dawsonite-Bearing Rocks in Well 22-1X

Rocks containing dawsonite in well 22-1X range from dolomudstones to dolomitic siltstones. They contain 26 to 46 wt % quartz, subequal amounts of plagioclase and potassium feldspar (6 to 13 wt % each), 1 to 2 wt % calcite, anhydrite, and gypsum, 10 to 15 wt % dolomite, 4 to 8 wt % hematite, 2 to 6 wt % kaolin, and 5 to 18 wt % illite, muscovite and biotite. These mineral abundances do not appear to differ in any significant way from rocks sampled in other wells that lack dawsonite.

The siltstones are dolomite cemented grain supported rocks that contain well-sorted silt to very fine sandsized grains in planar to rippled laminations. In contrast, the mica and silt grains in the dolomudstones are matrix-supported with fine-grained dolomite, iron oxide, and clay minerals. The dolomudstones appear to be intensely bioturbated, but they contain few sand or silt-filled burrows and laminations. Detrital micas, peloids and other clay-rich intraclasts are abundant and commonly accompanied by nodules of anhydrite and gypsum. All the rocks exhibit a strong red color caused by the hematite cement.

Textural relationships demonstrate that the dolomite and hematite represent early cementing phases (Fig. 10). The dolomite occurs as hematite stained microcrystalline rhombohedrons that line and fill pores. The dolomite was followed by the deposition of anhydrite and calcite cement, which are not stained by hematite. Gypsum, a common phase in rocks above and below the dawsonite zone encapsulates anhydrite, indicating it represents hydration of the earlier formed sulfate.

Dawsonite and kaolinite represent the youngest pore filling minerals (Fig. 11). Their occurrence has been confirmed by both X-ray diffraction and EDX analyses. The dawsonite occurs as radiating sprays of elongate to bladed prisms that comprise 5 to 17 weight percent of the samples. Although the dawsonite crystals are commonly spatially associated with corroded plagioclase and potassium feldspars, which are likely to have provided Al for crystal growth, it is also occasionally found growing on the surfaces of quartz grains. An unusual and distinctive feature of the dawsonite crystals are their hollow interiors. The external surfaces of the crystals, however, show no evidence of corrosion. We infer from these textures that the crystals grew outward by cannibalizing their own interiors.

Kaolinite is a common mineral in core samples from all five wells where it generally comprises up 2-7 weight percent of the rock. Scanning electron microscope images of core from 468 m clearly demonstrate that kaolinite is, at least in part, a late authigenic mineral. Here it occurs with dawsonite in intergranular pores as relatively coarse-grained books with individual plates exceeding 10 to 20 micrometers in size. The kaolinite also locally replaces dissolved potassium feldspar grains in the rock. The textural

relationships clearly demonstrate that both the kaolinite and dawsonite are younger than the dolomite and calcite cements on which they have grown. Although the kaolinite and dawsonite are not in contact with each other, the textural relationships displayed in Figure 11D suggest the kaolinite is younger than the dawsonite.

Rocks containing dawsonite are dolomite and calcite-cemented siltstones. Much of the porosity in these rocks, which is visually estimated to be approximately 20 %, appears to be the result of calcite dissolution. Dawsonite is commonly associated with patches of calcite and in places, fills pores that are similar in size to calcite fillings along coarse laminations in the siltstone. These siltstones may have initially been more porous than the overlying and underlying anhydrite-cemented mudstones that now contain 9 to 13 weight percent gypsum. These gypsiferous rocks appear to form a thick (~43 m) upper seal, and a thin (<3 m thick) lower seal.

Water Rock Interactions

The scarcity of dawsonite occurrences in sedimentary basins and its apparently limited distribution at Springerville-St. Johns is not consistent with thermochemical calculations suggesting dawsonite will deposit rapidly during the injection of CO_2 (e.g. Knaus et al., 2001). Instead, the field relationships suggest that the deposition of dawsonite occurs only under a relatively narrow range of geochemical conditions.

Based on their field studies of the Australian basins, Baker et al. (1995) concluded that the dawsonite was deposited by formation waters that had become acidified and enriched in HCO_3 as a result of the influx of CO_2 . They argued that these fluids would have been sufficiently aggressive to cause dissolution of feldspars and illitic clays, providing a ready source of Na and Al. Local sources for both the Al and Na are supported by the observation that the Na and K feldspars are commonly replaced by dawsonite (Baker et al., 1995, Heritsch, 1975; Wopfner and Hocker, 1987). A temperature of 25 to 35°C was suggested based on isotopic data (Baker et al., 1995).

Thermochemical modeling by Knaus et al. (2001) and Boram et al. (2003) indicate that high fugacities of CO_2 can lead to saturation of dawonsite. Knaus et al. (2001) simulated reactions between a brine, which was allowed to equilibrate with a gas consisting of 80 bar CO_2 and 10 bar H_2S , and a carbonate-bearing feldspathic sandstone. Deposition of dawsonite occurred after the fluid had equilibrated with the existing siderite and calcite and the pH had stabilized at 4.8. Dissolution of potassium feldspar at these slightly acidic conditions provided a source of Al. In the simulations, Si released during destruction of the feldspar precipitated as quartz and chalcedony.

In the following section we simulate interactions between the Springerville-St Johns waters and the siliciclastic sedimentary rocks that host the CO_2 reservoir. These results are constrained by the compositions of the waters, the presence of carbonate (dolomite, calcite) cements, evidence of feldspar dissolution, and the presence of late pore-filling dawsonite and kaolinite. The calculations were performed using the Geochemists Work Bench (Bethke, 1996) and version 8, release 6 of the Lawrence Livermore National Laboratory thermodynamic database.

Figure 12 shows there is a close relationship between mineral saturations in the groundwaters and the location of the CO_2 field. Saturation indices, given as log Q/K, indicate that all of the waters in the Springerville-St. Johns area are supersaturated with respect to calcite and dolomite but undersaturatured with respect to anhydrite and gypsum. The degree of supersaturation of dolomite is highest in the immediate vicinity of the CO_2 field. Similarly, saturation indices for gypsum are highest in the vicinity of the CO_2 field.

Water-rock interactions were simulated by adding CO_2 to water from Ridgeway Arizona Oil Corp. well 11-21 State and then reacting the water with the observed mineral assemblages. This water was taken as being representative of the deep water within the CO_2 field. Table 2 indicates that well 11-21 State water is substantially oversaturated with respect to dolomite but that the other carbonates are only slightly

oversaturated. This degree of oversaturation is unlikely within the reservoir. Consequently CO_2 was added to the water to reduce the pH to the point where dolomite was just saturated (e.g. log Q/K ~0). Quartz saturation was also stipulated in the simulations. The titration of 0.03 moles of $CO_2(g)$ per kg of water was required to just saturate the solution with respect to dolomite (Table 3). The fluid pH was reduced from 7.1 to 6.0 and the CO_2 fugacity increased from 0.07 to 0.92 bar.

This fluid was allowed to react with 10^{-8} moles each of albite, orthoclase, and anorthite feldspar in the presence of dolomite and quartz to examine the possible saturation of aluminous minerals. Figure 13 shows that kaolinite and muscovite rapidly achieved saturation, but that dawsonite remained undersaturated throughout the simulation.

The effect of a further increase in the fugacity of CO_2 on the stability of dawsonite is shown in Figure 14. In this simulation, one mole of CO_2 was added per kg of water in the presence of dolomite and quartz. The addition of the CO_2 lowered the pH of the solution from 7.1 to 5.0. The fluid was again allowed to react with albite, anorthoclase and orthoclase. Saturation of dawsonite was achieved after 0.7 moles of CO_2 had been added and the fugacity of CO_2 reached 20 bar. Kaolinite, however, remained undersaturated throughout the simulation.

The effects of incrementally reducing the fugacity of CO_2 from 20 to 0.92 bar in the presence of dolomite, quartz, albite, orthoclase, and anorthite feldspar are illustrated in Figure 15. As the fugacity of CO_2 in solution decreases, dawsonite becomes progressively undersaturated while the saturation index of kaolinite increases until stability is reached at a CO_2 fugacity of 16 bar. Further lowering of the CO_2 fugacity produces greater undersaturation with respect to dawsonite but has little effect on the solubility of kaolinite. These solubility relationships are consistent with the inferred mineral textures in well 22-1X State suggesting that the deposition of dawsonite preceded kaolinite.

The simulations provide a possible explanation for the common occurrence of kaolinite and overall scarcity of dawsonite in the Springerville-St. Johns rocks. These data suggest that the CO_2 fugacities were generally high enough to stabilize or deposit kaolinite but were too low to allow widespread deposition of dawsonite. High CO_2 fugacities in the dawsonite zone in well 22-1X could have been favored by effective upper and lower anhydrite- and gypsum-rich seals.

The source of the CO_2 in the Springerville-St. Johns field is enigmatic. Baker et al. (1995) noted that many sediment hosted-dawsonite occurrences are associated with volcanic or hydrothermal activity including those in the Australian Basins, the Permian Groeden Sandstone of northern Italy (Wopfner and Hocker, 1987) and the Shengli Oil Field of China (Du, 1982). Dawsonite from these occurrences contains C with similar isotopic compositions that are typically within a few per mil of 0.0, suggesting it has a magmatic origin. Although no isotopic data is available for Springerville-St. Johns, the association of the CO_2 field with young volcanic rocks and the presence of high He allow the possibility that the gases are derived from crustal or mantle sources tapped by through-going deep seated structures.

Summary and Conclusions

The Springerville-St. Johns CO_2 field represents an example of a relatively shallow gas reservoir that provides insight into the effects of CO_2 leakage to the atmosphere and low temperature interactions between CO_2 charged fluids and typical Colorado Plateau clastic sedimentary rocks. The production of CO_2 comes primarily from Permian siltones at depths of less than 900 m. CO_2 -bearing channel fillings lying uncomfortably on Precambrian granite at the base of the Permian section suggest that the reservoir is fed by gas migrating along through-going faults zones extending into deep crustal or mantle rocks. Individual production zones, however, are discontinuous, reflecting the combined effects of permeable horizons, access to crosscutting fractures and the efficiency of local seals.

Dissolution of CO_2 into the local groundwaters has had a profound effect on their chemical character and on their interactions with the rocks that host the CO_2 field. The resulting acidity has produced chemically aggressive waters capable of rapid corrosion of metal drill pipe. There is a clear geochemical signature over the CO_2 field. Waters in the immediate vicinity of the field are enriched in HCO_3 and SO_4 and show the greatest degree of saturation with dolomite and gypsum, common cements in the reservoir rocks. These waters are commonly Na-K HCO_3 , Na-K HCO_3 -SO₄ and Ca Cl in character.

Investigations of the reservoir rocks within the CO₂ field have documented several generations of authigenic minerals. Early pore-filling cements consist of dolomite, hematite, calcite, anhydrite and gypsum. These minerals are overprinted by dawsonite and kaolinite. Kaolinite is common throughout the reservoir, but dawsonite has so far been observed only in a single relatively narrow interval of siltstones. Textural relationships indicate that the Al was provided by the dissolution of detrital feldspars. Na may also have been derived from the feldspars. Interactions between the reservoir rocks and basin fluids from the CO₂ field were simulated. The models indicate that kaolinite will become saturated at a CO₂ fugacity of <1 b but that dawsonite will not precipitate until the CO₂ fugacity reached 20 b. The high CO2 contents of the fluids that precipitated dawsonite may reflect the presence of effective low permeability seals.

Spectacular symmetrical domes ranging up to 610 m in diameter and extensive sheets of travertine up to 6.4 by 3.2 km in area record a long history of CO_2 leakage to the surface. Bicarbonate-rich springs and pools are found within travertine deposits on the valley floors close to the elevation of the modern Little Colorado River, but large terraces of travertine are also perched up to 60 m above the valley floor. The present depositional rates appear to be low and relatively insignificant compared to the amount of past deposition and there is no evidence of CO_2 exsolving from the pools and springs.

Several factors may have contributed to the decline in travertine activity. These include lowering of the water table, significantly diminished outflow of CO_2 -charged waters due to a drier climate and a reduced flux of CO_2 at depth resulting in lower dissolved CO_2 in the outflowing water. The occurrence of dawsonite suggests that CO_2 partial pressures were higher in the past.

At the time of dawsonite deposition, and perhaps soon after CO_2 began flooding into the region, the subsurface fluid system could have been over-pressured by the influx of gas which caused major outflows of CO_2 -saturated waters producing the travertine domes and plateaus. As the partial pressure of CO_2 declined, the degree of over-pressuring diminished and the newly formed domes became perched above the receding groundwater table. Kaolinite replaced dawsonite as the dominant alteration mineral. Today the pressure is close to hydrostatic from the elevation of the Little Colorado River, and the outflow of water from the CO_2 system at depth is greatly reduced. The absence of obvious CO_2 exsolution in the present day springs is attributed to lateral outflow from the main CO_2 upflow zone further east, and loss of CO_2 along the flow path. The Permian Kaibab-Glorieta sandstone units and the underlying Supai Formation act as one aquifer that extends at depth at least 30 km to the east and south of the travertine area

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| | | | Salado | |
|-------------|----------|----------|------------|-------------|
| | P-12 | P-14 | Springs | 11-21 State |
| Na | 140 | 330 | 340 | 804 |
| Κ | 15 | 32 | 26 | 174 |
| Ca | 130 | 290 | 330 | 110 |
| Mg | 39 | 55 | 63 | 232 |
| Fe | | 0.84 | 0.27 | 18.3 |
| Sr | 2.1 | 5.4 | 3 | |
| В | 0.24 | 0.59 | 0.75 | |
| SiO2 | 19 | 15 | 13 | |
| HCO3 | 186 | 288 | 336 | 1190 |
| SO4 | 210 | 640 | 610 | 1540 |
| Cl | 140 | 410 | 660 | 483 |
| F | 2 | 2.6 | 2.6 | |
| As | 0.008 | 0.032 | | |
| TDS | 840 | 2100 | 2150 | 4210 |
| pН | 7 | 6.5 | | 7.1 |
| | Tucson | Tucson | | Ridgeway |
| | Electric | Electric | | Arizona |
| Data Source | Power | Power | This Study | Oil Corp. |

Table 1. Chemical analyses of the Tucson Electric Power Co. wells (P-12, P-14), Salado Springs, and Ridgeway Arizona Oil Corp. well 11-21 State.

Table 2. Mineral saturations for water from well 11-21 State (see Table 1).

| Mineral | Log Q/K |
|-----------|---------|
| Dolomite | 2.2667 |
| Calcite | 0.3752 |
| Magnesite | 0.2627 |
| Gypsum | -1.008 |

Table 3. Mineral saturations after the addition of 0.03 moles of CO_2 per kg water from well 11-21 State. Compare saturation indices with data in Table 2.

| Mineral | Log Q/K |
|-----------|---------|
| Dolomite | 0.0062 |
| Calcite | -0.7548 |
| Magnesite | -0.8678 |
| Gypsum | -1.0071 |



Fig. 1. Location of natural CO_2 reservoirs within the Colorado Plateau and Southern Rocky Mountain Region of the U.S. (after Allis et al., 2001). The inset shows the location of the Springerville-St Johns region illustrated in Figure 2.



Fig. 2. Location of the Springerville-St.Johns CO_2 field. Only the names of wells discussed in the text are shown.



Fig. 3. Generalized geologic section of the Springerville-St. Johns area (after Rauzi, 1999).



Fig. 4. Travertine deposits in the Springerville-St. Johns area. A) Travertine sheets and pool adjacent to Salado Springs. B) A small well preserved travertine dome on the valley floor. C) Interior of a large travertine dome located south of Salado Springs (see Fig. 4D). D) Areal view of the Salado Springs area showing extensive travertine sheets north of the springs and a large dome to the south. The dome's central vent is clearly visible. E. Travertine sheets on the bluff above the Little Colorado River (lower left and center of photo).



Fig. 5. Relationships between pressures and elevations in the Springerville-St. Johns area. Wells from the CO_2 field define a trend with a pressure intercept close to 1830 masl, consistent with the elevation of springs and pools adjacent to the Little Colorado River. Symbols as in Fig. 2. West of this area, the pressure intercept is close to 1525 masl. Abbreviations: TEPC = Tucson Electric Power Co.



Fig. 6. Northwest-southeast cross section of the Springerville-St. Johns area. See Figure 2 for the location of the cross section. The sections includes the area of the travertine deposits and the CO_2 field (in the structural high left of Salado Springs).



Fig. 7. Locations of water samples used in this study.



Fig. 8. Piper plot of water analyses.



Fig. 9. Distribution of water types in the Springerville-St. Johns area.



Fig. 10: Photomicrograph of early diagenetic cements. Dolomite and hematite were deposited first, followed by calcite and anhydrite. The anhydrite has been replaced by gypsum. From a depth of 462 m in well 22-1X State. Taken under crossed nicols.



Fig. 11. Scanning electron microscope backscattered electron images showing authigenic dawsonite and kaolinite from a depth of 468 m in well 22-1X State. A) Dawsonite growing on weathered potassium feldspar. The feldspar displays dissolution microporosity. B) Dawsonite prisms showing characteristic hollow interiors. The dawsonite crystals have grown on a grain of detrital quartz. C) Close-up of a hollow dawsonite crystal growing on the surface of a silt grain. There is no corrosion of the crystal's exterior. D) Pore filling kaolinite and dawsonite. A partially dissolved grain of detrital feldspar projects into the pore space that is lined with early augithenic dolomite. Abbreviations: Daw = dawsonite; do = dolomite; Fld = feldspar; Kaol = kaolinite.



Fig. 12. Anion concentrations (in ppm) and mineral saturations (as log Q/K) in the Springerville-St. Johns area. A) Concentrations of HCO₃. B) Concentrations of SO₄.



Fig. 12 cont. C) Degree of dolomite saturation. Dolomite is strongly supersaturated in the vicinity of the CO_2 field. D) Degree of gypsum saturation. Although gypsum is undersaturated throughout the area, the highest saturation indices are associated with the CO_2 field.



Fig. 13. Saturation state of aluminous minerals after adding 0.03 moles of CO2 per kg of water from well 11-21 State. Reactions with and 1e-8 moles of albite, anorthite, and orthoclase in the presence of quartz and dolomite were modeled. Reaction (Rxn) progress is plotted on the X-axis.



Fig. 14. Effect of adding 1 mole of CO_2 per kg of water on the saturation state of aluminous minerals. Other constraints are the same as were used in the simulation shown in Figure 14. Saturation of dawsonite occurred when the CO_2 fugacity reached 20 bar.



Fig. 15. Effect of reducing the fugacity of CO_2 from 20 to 0.92 bar on the saturation states of the aluminous minerals. Other conditions as in the preceding simulations. Kaolinite saturation was reached at a CO_2 fugacity reached 16 bar.