Delineation of Magnesium-rich Ultramafic Rocks Available for Mineral Carbon Sequestration in the United States

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Abstract

The 2005 Intergovernmental Panel on Climate Change report on Carbon Dioxide Capture and Storage suggested that a major gap in mineral carbon sequestration is locating the magnesium-silicate bedrock available to sequester CO\textsubscript{2}. It is generally known that silicate minerals with high concentrations of magnesium are suitable for mineral carbonation. However, no assessment has been made covering the entire United States detailing their geographical distribution and extent, or evaluating their potential for use in mineral carbonation. Researchers at Columbia University and the U.S. Geological Survey have developed a digital geologic database of ultramafic rocks in the continental United States. Data were compiled from varied-scale geologic maps of magnesium-silicate ultramafic rocks. These rock types are potentially suitable as source material for mineral carbon-dioxide sequestration. The focus of the national-scale map is entirely on suitable ultramafic rock types, which typically consist primarily of olivine and serpentine minerals. By combining the map with digital datasets that show non-mineable lands (such as urban areas and National Parks), estimates on potential depth of a surface mine, and the predicted reactivities of the mineral deposits, one can begin to estimate the capacity for CO\textsubscript{2} mineral sequestration within the United States.

Keywords: Mineral Carbon Sequestration; Ultramafic Rocks; Serpentine; Olivine; Resource Assessment

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doi:10.1016/j.egypro.2009.02.322
1. BACKGROUND

Mineral carbon dioxide sequestration is a proposed greenhouse gas mitigation technology whereby \( \text{CO}_2 \) is disposed of by binding it with calcium or magnesium to form a solid magnesium or calcium carbonate product.

The reaction offers virtually unlimited capacity to permanently store \( \text{CO}_2 \) in an environmentally benign form via a process that takes little effort to either verify or monitor. The technology has its origins in the 1990's with the initial idea credited to Seifritz and its initial development by Lackner and others at Los Alamos National Laboratory [1, 2].

The 2005 Intergovernmental Panel on Climate Change Special Report on Carbon Dioxide Capture and Storage suggested that a major gap in mineral carbon sequestration is locating the magnesium-silicate bedrock available to sequester \( \text{CO}_2 \).

1.1. Minerals Suitable for Mineral Carbon Sequestration

Potential mineral ores should be abundant, concentrated in magnesium, and reactive with respect to the process being utilized. Silicate minerals are the most abundant mineral on the earth's crust and make an obvious choice for magnesium ores. Calcium silicates are also suitable but far less abundant.

Silicate minerals with high concentrations of magnesium are referred to as mafic minerals. Specifically, the magnesian minerals olivine, orthopyroxene, and clinopyroxene contain less than 45% weight content silica; rocks containing high proportions of these minerals are called ultramafic rocks, and are named depending on the proportions of these minerals in the rock (wherlite, lherzolite, harzburgite, etc., See Figure 1). Ultramafic rocks often undergo metamorphic hydration to produce serpentinites, also potentially suitable for mineral carbonation.

This study focuses on the location of ultramafic rocks as a potential resource base for a mineral carbon sequestration process. Example carbonation reactions for serpentine and olivine are:

- \textit{Serpentine}: \[
\frac{1}{3} \text{Mg}_2\text{Si}_3\text{O}_4(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{2}{3} \text{SiO}_2 + \frac{2}{3} \text{H}_2\text{O}
\]
- \textit{Olivine}: \[
\frac{1}{2} \text{Mg}_2\text{SiO}_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{1}{2} \text{SiO}_2
\]

![Figure 1. IUGS Classification diagram for ultramafic rocks based on modal percentages of three mafic minerals (olivine, orthopyroxene, and clinopyroxene). [3]](image-url)
1.2. Ultramafic Complexes

The most abundant sources of ultramafic rocks occur in orogenic zones that are the result of collisions between crustal and oceanic tectonic plates. Two types of ultramafic rocks are found in orogenic zones: Alpine-type ultramafics and ultramafic volcanic arc plutons. Intracratonic ultramafic bodies (formed in the interior of a continental plate) include layered intrusions and komatiitic metavolcanic rocks [Wyllie, 1967]. All of these rocks have separate petrologic and tectonic histories and as such exhibit differences in location, mineralogy, and mineralogical distribution (Table 1).

1.3. Orogenic Alpine Ultramafic Rocks

Alpine-type ultramafic rocks were once part of the mantle below the ocean-floor crust. To arrive at their continental location, ocean crust has been obducted (thrust up) onto continental crust as oceanic crust collided with continental crust. The suite of rocks resulting from this process is known as an ophiolite [4]. These are typically located along active or previous convergent plate boundaries. In the United States, these rocks constitute the majority of ultramafic rock exposures, located primarily in north-south-trending belts in the east and west coast states (Figure 2).

The ultramafic section of the ophiolitic suite is divided into two categories, based on the texture of the material. Tectonite forms the bottom section and consists of dunite pods and lenses in harzburgite or lherzolite. The tectonite layer grades upward into what is known as the cumulate section, in which olivine crystals form the dominant phase. Both of these sections will show varying ranges of serpentinization (conversion of the olivine and pyroxenes to serpentine) [4].

1.4. Orogenic Volcanic Arc Plutons

Ultramafic volcanic-arc plutons are concentrically zoned ultramafic rocks that were formed as the feeder tubes of subvolcanic magma chambers in volcanic-arc complexes. The arcs are formed as ophiolite is accreted onto continental crust, and the plutons occur in orogenic zones in proximity to, or amidst, ophiolite complexes. The plutons generally contain a core of unserpentinized dunite surrounded by successive zones of serpentinized ultramafic and mafic rocks. Whereas ultramafic volcanic arc plutons constitute a much smaller fraction of ultramafic material compared to the Alpine-type, they are notable for their high concentrations of unaltered dunite, a potential source of concentrated olivine [5].

1.5. Intracratonic Mafic to Ultramafic Layered Intrusions

The last major ultramafic rock types are the intracratonic layered intrusions. These formations are the fossil magma chambers below continental crust in which magma slowly crystallized and differentiated via gravity settling. The tectonic setting of these intrusions is not fully understood, but there is evidence that they are associated with crustal rifting zones, in areas where the continental crust is relatively thin, thereby allowing for the transport of magma closer to the surface.

Minerals in layered intrusions are concentrated into layers as the result of crystal settling and chemical differentiation processes in the magma chamber. Layers often occur in cycles, with many stacked layer cycles comprising a series in the intrusion. An ultramafic series, for example, may contain alternating layers of dunite, harzburgite, and orthopyroxenite. The layers themselves are often laterally continuous across the length of the intrusion and thus can present a relatively simple opportunity for resource exploitation [3].
1.6. Intracratonic Komatiitic Metavolcanic Rocks

The last major ultramafic rock type are associated with Archean komatiitic metavolcanic rocks and related subvolcanic intrusive rocks (Day and others, 1994; Snyder and others, 1989; Sims, 1992). Peridotite and minor amounts of dunite cumulates form by crystal settling from thick basaltic, pyroxenitic, and peridotitic komatiite flows and subvolcanic sills. Serpentine minerals, talc, chlorite, magnesite, anthophyllite, and tremolite form in the basal parts during metamorphism. These flows and sills are commonly a few meters to 0.5 km thick and may be exposed over 1-5 km. They are typically associated spatially with thick submarine tholeiitic basalts sequences. Their tectonic environment of formation remains controversial, ranging form ocean floor volcanism related to mantle plumes to compressional and tensional arc environments.

Table 1. Ultramafic complex types in the U.S. Modified from [6].

<table>
<thead>
<tr>
<th>Geologic Setting</th>
<th>Complex Type</th>
<th>Description</th>
<th>Distribution of Ultramafic Minerals</th>
<th>U.S. Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpine Type</td>
<td>Tectonite section contains pods of dunite, whereas cumulate section contains layers of dunite. Dunite is often highly serpentinized</td>
<td>East and west coast United States</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volcanic Arc Plutons</td>
<td>Intrusion formed in an island arc complex accreted onto continental crust</td>
<td>Concentrically zoned mineral distribution with a dunite core surrounded by successive zones of clinopyroxenite and orthopyroxenite. Variable serpentinization, increasing outwards from dunite core</td>
<td>East and west coast United States, Duke Islands, Alaska</td>
<td></td>
</tr>
<tr>
<td>Intracratonic</td>
<td>Layered Intrusions</td>
<td>Large intrusions formed under continental crust</td>
<td>Alternating layers of peridotite and pyroxenite extending laterally over the length of the intrusion. Variable serpentinization with the most alteration along faults and shear zones</td>
<td>Stillwater, Montana</td>
</tr>
</tbody>
</table>

Figure 2. Map of ultramafic rock bodies (black) suitable for carbon sequestration, drawn from the dataset discussed in this work. Areas are shown with thick outlines for visibility.
2. ULTRAMAFIC ROCKS IN THE UNITED STATES

Exposed ultramafic rocks are most concentrated on the eastern and western coasts of the United States, where past convergent plate boundaries resulted in the emplacement of ophiolites and volcanic arc terranes. The rocks exist predominantly in ophiolite complexes, along with a handful of volcanic arc plutons. Ultramafic rocks of the interior United States are sparse, but include one major zoned intrusive type body in Montana (the Stillwater Complex), a suite of komatiitic metavolcanic rocks in Minnesota, Wisconsin, and Michigan, and a small zone of serpentinite in central Texas (Figure 2).

2.1. Ultramafic Rocks of the Western United States

The ultramafic rocks of the western United States, particularly in California, Oregon, and Washington [Irwin 1977, 1979], likely host the largest bodies of both olivine and serpentine in the United States. They consist of multiple ophiolite and arc pluton assemblages emplaced during multiple orogenic events of the late Paleozoic and Mesozoic Eras [Bailey et al. 1964]. The ultramafic bodies of the west coast have been extensively studied for their geological importance, as well as their economic importance as a resource base for mineral resources, including aggregate (crushed stone), asbestos, chromite, nickel, tale (soapstone), and olivine foundry sand.

The rocks of the western United States can be separated into 5 distinct geologic zones. From north to south, they are: (1) The ophiolitic terranes of western Washington, (2) the Canyon Mountain complex of eastern Oregon, (3) the Klamath-Trinity region of the western California-Oregon border, (4) the western foothills of the Sierra Nevada of California, and (5) the Coast Ranges of California [7, 8].

2.2. Ultramafic Rocks of the Eastern United States

Ultramafic rocks exist in exposures along the entire Appalachian belt of eastern North America, from Newfoundland in Canada to Alabama in the southeastern United States [Williams and Talkington 1977]. They are generally taken to be ophiolitic in origin, formed during the closing of the Iapetus Ocean (a precursor to the Atlantic) during much of the Paleozoic era. A previous resource assessment for ultramafic rocks suitable for mineral sequestration on the East Coast was performed in 2000. In this study, the ultramafic rocks of the eastern United States are divided into three main sections: (1) ultramafic rocks of Vermont, (2) the Baltimore and Liberty Complexes of the PA-MD-DC region and (3) dunites of western North Carolina. [9-11]

2.3. Ultramafic Rocks of the United States Interior

The largest known layered ultramafic intrusion in the United States is the Stillwater Complex of southwestern Montana. A peridotite unit spans the 48 km length of the intrusion, which contains olivine and pyroxene minerals 20-100% serpentinized. [12, 13]

In Texas, a few small serpentinite bodies are located in Gillespie, Blanco, and Llano counties. [14]

Our study also includes ultramafic rocks in Minnesota, Michigan, and Wisconsin that are mostly concealed by a thin veneer of glacial deposits. Small serpentinite outcrops are associated with Archean metamorphosed volcanic rocks and related subvolcanic intrusive rocks in northern Minnesota and Wyoming (Day and others, 1994; Snyder and others, 1989). Similar rocks may occur in northern Michigan and Wisconsin in Archean and some Early Proterozoic metavolcanic enclaves (e.g. Sims, 1992). Because these rocks are mostly covered by glacial deposits, their shallow subsurface extents were mapped from interpretation of aeromagnetic data in combination with sparse outcrop and drill hole data (Day and others, 1994). [12]
3. FUTURE WORK

The map and geologic database discussed will be released as a U.S. Geological Survey Digital Data Series publication upon completion and will include ultramafic bodies in Alaska and Puerto Rico. An analysis will be performed providing initial estimates on the sequestration capacity, integrating limitations such as current land use and proximity to CO$_2$ sources. Potential uses for the data include estimating the resource base available for mineral CO$_2$ sequestration, assessing its potential CO$_2$ storage capacity, and preliminary siting for pilot and industrial sequestration projects.

References