

Geological sequestration of carbon dioxide in Deccan basalts: preliminary laboratory study

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Laboratory experiments to probe the carbon dioxide sequestration potential of picritic basalts from the Deccan Basalt volcanic province, Maharashtra are reported. Growth of certain secondary carbonates is clearly seen over the surface of picritic basalts, reacted with water and carbon dioxide in its supercritical condition. The reactions were kept for about 5 months duration at a temperature and pressure of 100°C and 60 bar of CO₂ respectively. Handpicked soft grains of secondary carbonates were characterized using infrared spectroscopy and the observed signatures in two of the picritic basalt samples (IGP-40 and IGP-29) match well with ankerite (Fe-carbonate), with negligibly small amounts of released SiO₂. While in another sample (IGP-36), the secondary carbonates have comparatively larger amounts of SiO₂.

Keywords: Carbon dioxide, geological sequestration, picritic basalts, secondary carbonates.

INCREASING levels of greenhouse gases (GHGs) such as carbon dioxide in the atmosphere are currently of great concern. Usage of fossil fuels is necessary to meet the ever-increasing energy requirements for technological advancements. Greater urbanization is reducing the forest cover (the major source for terrestrial CO₂ sequestration), causing natural atmospheric imbalance. Thus, the need of the hour is to probe ways and means of managing the levels of GHGs in the atmosphere¹. Mineral carbonation, in which CO₂ is reacted with primary silicate minerals to form the respective solid and secondary iron, magnesium and calcium carbonates, is one of the sequestration methods being investigated²⁻⁴. This process is environmentally benign and the resultant mineral carbonates are stable over geological timescales. The technological challenge is to optimize the reaction rate to maximize CO₂ sequestration in a selected geological set-up. The idea of applying mineral carbonation reaction for CO₂ storage was first proposed by Seifritz⁵. Since then active research work is being carried out worldwide on a number of geological materials²⁻⁸.

Immense basalt flows of Cretaceous–Tertiary ages spread over vast domains in the world are recognized as

playing an important role in the global carbon cycling. Large igneous provinces represent immense outpourings of mafic (iron- and magnesium rich) magmas with subordinate ultramafic flows, and include continental flood basalts, volcanic passive margins and oceanic plateaus⁹. Shallow basaltic rocks with well-developed interflow structures serve as regional aquifer systems in several regions worldwide, e.g. Columbia River Basalt Province, USA. Hence, these basalt formations appear to have the necessary silicate mineralogy, characteristic composition, storage capacity, internal structure and permeability to support geological sequestration of CO₂. The Deccan Volcanic Province (DVP) in India is one of the favourable locations and appears to have similar characteristics like the Columbia River Basalt Province¹⁰. Origin of the DVP is generally viewed as an upwelling of deep mantle plumes beneath the Indian subcontinent dating back to the Cretaceous/Tertiary boundary^{9,11,12}. The DVP is composed of 13 different flows on an average, with typical tholeiitic compositions and occasionally inter-layered picritic basalts, and consisting of columnar, massive, vesicular, amygdaloidal, tuffaceous and brecciated varieties^{11,12}. In order to ascertain its utility in CO₂ sequestration, it is highly desirable to understand its reactivity with CO₂ under various *P* and *T* conditions. In this communication, we describe the first laboratory results obtained on reacting the picritic basalts from DVP with supercritical CO₂. These are preliminary experiments aimed at establishing the chemical reactivity of these basalts and characterizing the secondary carbonates. Quantitative estimates would be presented in our future work.

The picritic basalts occur as interlayered flow units within the sequence of tholeiite basalts in the Igatpuri Formation¹². These picritic basalts, collected from different parts of the flow unit, are medium-grained with porphyritic olivine and clinopyroxene set in a ground mass of fine-grained clinopyroxene ± olivine, ± plagioclase and titanomagnetite. Some porphyritic olivine and clinopyroxene are pseudomorphically altered to serpentine ± chlorite.

Laboratory experiments to establish the chemical reactivity of picritic basalts from the DVP were conducted at ~100°C and a CO₂ pressure of about 60 bar. Indigenously fabricated titanium pressure vessels, having minimum wall thickness of 7 mm, an internal volume of ~25 ml and tested to hold a gas pressure of 150 bar, were used in our long-term chemical reactivity experiments. Picritic basalt chips (25 g) of ~2–3 mm size were reacted with CO₂ gas and 25 wt% H₂O for about 5 months duration.

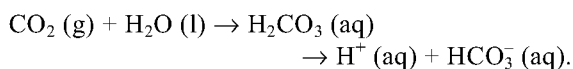
The whitish cluster of crystals (softer in nature) grown over the picritic basalt chips were carefully separated and analysed by Fourier Transform Infrared (FTIR) spectroscopy. FTIR studies were carried out on a Thermo-Nicolet-make NEXUS FTIR spectrometer (with sealed and desiccated optics), using a thermo-electrically cooled deuterated triglycine sulphate detector, extended range

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KBr (XT-KBr) beam splitter, and a dual source working in the wavenumber range 375–12,500 cm^{-1} . The conventional KBr pellet method has been followed to study the fundamental modes in the wavenumber range 400–4000 cm^{-1} , using NEXUS Ever-Glo source¹³.

Table 1 shows the major element chemical compositions of the picritic basalts used in the present investigation. The total percentages of Ca, Mg and Fe oxides in these picritic basalts are around 35 wt% and volatiles are less than 2 wt%. Further, the FTIR spectrum of virgin samples is dominated by a peak around 1080 cm^{-1} , indicating the dominance of SiO_2 . Broader and weaker H_2O peaks are also observed around 3400 cm^{-1} , and absence of sharper peaks in this region clearly indicates the absence of structural (OH) in these virgin picritic basalts, and the water could be mostly localized within the pores/grains.

Direct and dry carbonation process involves the reaction between solid Ca/Mg-silicates and gaseous CO_2 , where the products are carbonates and silica. However, the reaction rates are extremely slow and the challenge is to optimize the conditions for this process so as to assess the potential of the chosen basaltic composition for carbon dioxide sequestration. It has been experimentally observed that the presence of water could significantly increase the rate of carbonation in Ca/Mg silicates. The aqueous mineral CO_2 sequestration process operates in three steps simultaneously in one reactor. First, CO_2 is dissolved in a water phase resulting in a mild acidic environment with HCO_3^- as the dominant carbonate phase as shown by the reaction:



Secondly, Ca/Mg gets leached from the primary mineral matrix facilitated by the protons present according to the reaction:

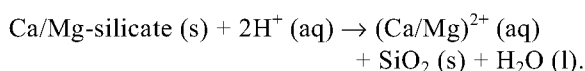


Table 1. Major element composition of picrites

Wt%	IGP-40	IGP-29	IGP-36
SiO_2	48.41	48.52	48.28
Al_2O_3	11.46	11.16	11.72
Fe_2O_3	13.76	14.38	14.41
MnO	0.16	0.17	0.17
MgO	11.21	11.29	10.98
CaO	10.32	9.41	8.89
Na_2O	1.50	1.57	1.65
K_2O	0.30	0.43	0.48
TiO_2	1.58	1.41	1.41
P_2O_5	0.19	0.19	0.19
Sum	98.90	98.54	98.17

Finally, Ca/Mg-bearing secondary carbonates are precipitated in the process due to the reaction:

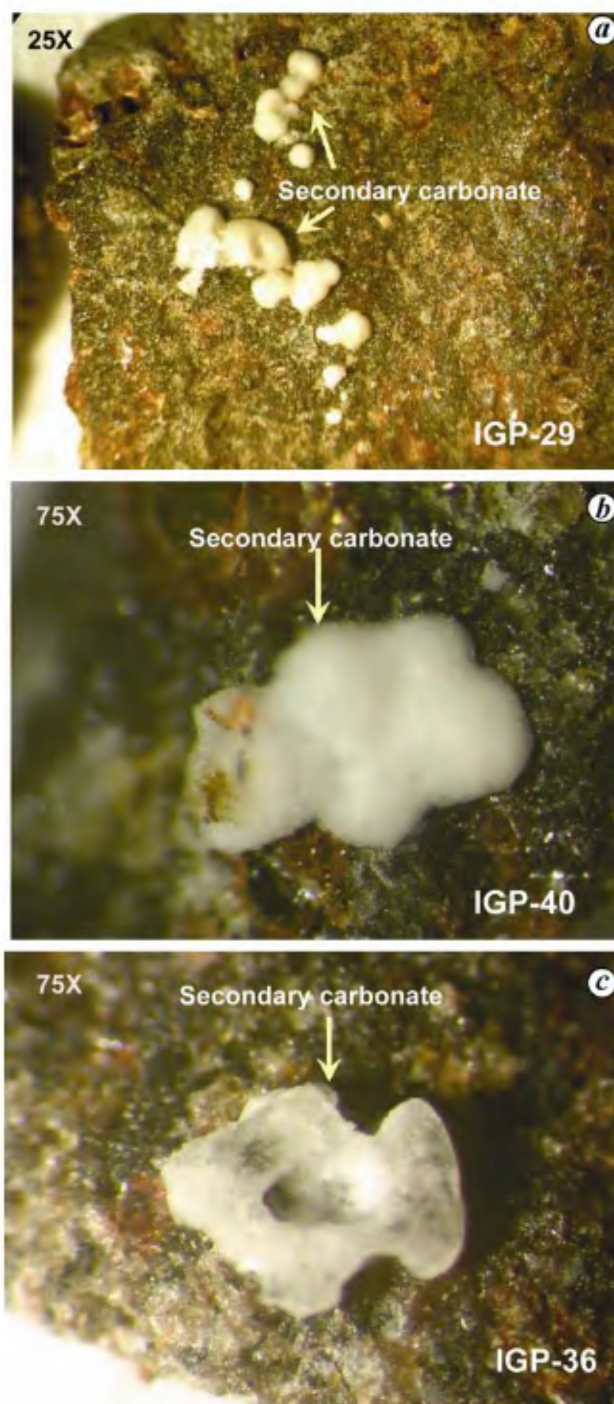
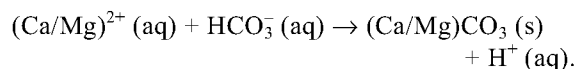


Figure 1 a–c. Megascopic photograph showing formation of secondary carbonates (whitish globules and fine-grained, whitish, intergranular cementing material – indicated by arrow) on the picrite samples. Reddish grains are porphyritic olivines set in a dark coloured clinopyroxene and titanomagnetite-bearing matrix.

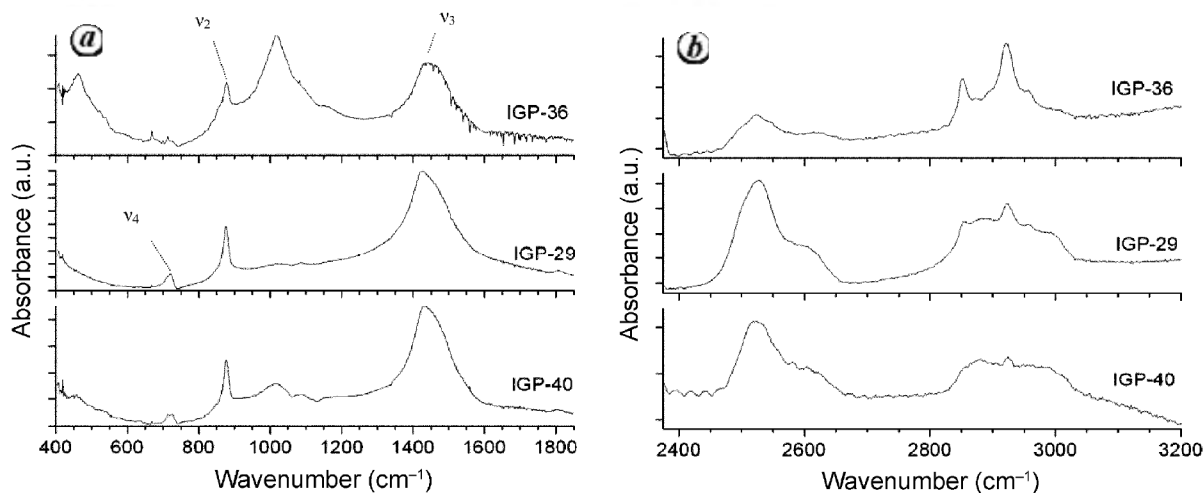


Figure 2. FTIR spectra of secondary carbonates in fundamental (a) and overtone (b) regions (a.u., arbitrary units).

The first step to maximize the reaction rate is a careful selection of process conditions such as particle size, temperature and pressure of CO₂. As already stated, we have taken picritic basalt chips of about 2–3 mm size, which were reacted with CO₂ in its supercritical state at a reaction temperature of 100°C. The CO₂ sequestration under these experimental conditions was through aqueous mineralization as the process also involved around 25 wt% H₂O.

The photomicrographs (Figure 1 a–c) for all the reacted samples clearly show well-grown carbonate phases as secondary minerals. It is also observed that the carbonate phases have cemented the intergranular spaces in the reacted picritic basalts. Small portions of the secondary minerals were carefully separated and analysed by FTIR spectroscopy. The characteristic free carbonate-ion modes around 1415 cm⁻¹ (asymmetric stretch – ν₃); 879 cm⁻¹ (out-of-plane bending – ν₂) and 680 cm⁻¹ (in-plane bending – ν₄) are IR-active and have been used for identifying the carbonate ion¹⁴. The symmetric stretching mode (ν₁) occurring around 1063 cm⁻¹ is Raman-active and IR-inactive. Figure 2 shows the recorded FTIR spectra of the reactants. It is evident that the characteristic carbonate peaks are clearly observed in IGP-40 and IGP-29. The asymmetric stretching mode (ν₃) for these two samples is observed at 1435 and 1427 cm⁻¹. Similarly, the bending modes are also observed at 877 and 876 cm⁻¹ (ν₂) as well as 725 and 721 cm⁻¹ (ν₄) respectively. The spectral features find a close match with (~80%) ankerite. Other weaker bands around 1083 and 1018 cm⁻¹ could be due to SiO₂. Such bands are relatively weaker in IGP-29. The additional band at 713 cm⁻¹, observed¹⁵ in ν₄ mode region, could be because of excess CaCO₃ and/or due to SiO₂. Stronger asymmetric stretching mode of Si–O network around 1019 cm⁻¹, typical of SiO₂, is clearly seen in IGP-36 along with carbonate signatures. Other weaker second-order modes typical of carbonate around 1800 cm⁻¹, and

doublet around 2550 and 2950 cm⁻¹ are also clearly observed as shown in Figure 2 b. Absence of FTIR modes in the region 3200–3600 cm⁻¹ clearly reflects the non-existence of hydroxyl (molecular or structural) groups in the carbonates in all the samples investigated in the present study.

In summary, we have demonstrated the reactivity of picritic basalts from Igatpuri Formation, DVP, for CO₂ sequestration. Secondary carbonates formed due to mineral carbonation reactions were characterized to be ankerites using FTIR spectroscopy. Our future studies will be focused on quantifying the CO₂ sequestration capability of basalts and associated ultramafic rocks of the DVP.

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ACKNOWLEDGEMENTS. We thank Dr V. P. Dimri, Director, NGRI, Hyderabad for encouragement and permission to publish this paper. P.S.R.P. and S.N.C. thank DST, New Delhi for financial support. We also thank Prof. S. F. R. Khadri, Head, Department of Geology, SGB Amaravati University, Amaravati for discussions during field work.

Received 9 June 2008; revised accepted 8 December 2008

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