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Stable isotopes of lithium as indicators of coal seam gas-bearing aquifers

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Abstract

In this study lithium isotopes were used in combination with hydrochemistry to investigate interactions between coal-seam-gas bearing sedimentary bedrock aquifers and surrounding basalt and alluvial aquifers in a large catchment in eastern Australia. Understanding groundwater transport and aquifer connectivity is critical to managing coal seam gas (or coal bed methane) developments, because large volumes of water need to be extracted in order to release the sorbed gas; however, to date lithium isotopes have not been applied to coal seam gas groundwater management problems and no information on the δ^7Li of coal or coal-seam groundwater is available. Li/Cl and Li/Na ratios in the coal-bearing and sedimentary bedrock aquifers are distinct (>0.0001) from alluvial and basalt aquifers (<0.0001). Preliminary δ^7Li results for coal measure samples are typically between 7 and 11‰; many of these samples also contain methane, and can therefore be expected to be influenced by coal and the early stages methanogenesis. Interestingly the coal measure with lowest δ^7Li value occurs in an area where the coal measures outcrop and direct recharge is likely, with nearby basalt groundwater having much higher δ^7Li values (δ^7Li>18‰). Preliminary lithium isotope results show that δ^7Li may be effective in distinguishing groundwater flow paths in the coal-bearing aquifer from basalt aquifers, and from a transitional zone between the alluvium and underlying coal measures. Further lithium isotope analysis is being carried out to: a) compare the δ^7Li between alluvial, basalt and coal-bearing aquifers to further investigate aquifer connectivity; b) to describe δ^7Li for CSG production waters with low- and high-methane groundwater in the coal-bearing aquifer; c) to describe the δ^7Li from coal and basalt leachate.

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Keywords: "stable isotopes of lithium; coal seam gas (coal bed methane); aquifer interaction"

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1. Introduction

Coal seam gas (CSG) refers to sorbed gas, predominantly methane, held under pressure in underground coal seams. The gas may be biogenic or thermogenic. There is growing interest in commercial production of this resource globally. The extraction process requires large volumes of groundwater to be extracted from the coal seams so that the sorbed gas is released. This water extraction process raises concerns about aquifer connectivity, particularly where other important groundwater resources, such as those used for agriculture, occur in adjacent aquifers. There is a need for effective indicators of aquifer connectivity to be described that allow interactions between aquifers to be described and flow paths within and between aquifers to be delineated.

The stable isotopes of lithium (δ^7Li) have successfully been applied in other studies to investigate groundwater flow paths and aquifer interaction, and δ^7Li shows promise as an effective aquifer connectivity indicator in settings where methanogenesis is occurring because lithium isotopes do not undergo fractionation at redox or pH conditions, or under biologically mediated processes[1,2,3]. The fractionation of lithium isotopes in clays and brines has allowed δ^7Li in production waters from oil and gas producing wells in shale and shale-bearing sedimentary basins to be successfully applied to investigate fluid migration and the origin of brines[4,5,6] (see Figure 2 for δ^7Li range of these waters). However, to date no work has been performed on lithium isotopes in coal seams, particularly those associated with CSG. Coal deposits have also been shown to be a promising source of rare metals, including lithium[7,8], and this suggests that groundwater from coal-bearing aquifers may have distinct lithium isotope signatures.

In this study, lithium isotopes, in combination with major and minor trace elements, are used to investigate flow paths within and between coal-bearing sedimentary bedrock aquifers, basalt aquifers and alluvial aquifers in the Condamine River catchment, south east Queensland, Australia. The upper Condamine River alluvium is an important agricultural groundwater resource and is flanked by a large Neogene alkaline olivine basalt extrusion and outcrops of the Walloon Coal Measures (WCM) and other Jurassic sedimentary bedrock of the Surat and Clarence-Moreton basins (Figure 1). The sedimentary deposits are comprised of sandstones, siltstones, mudstones and coal, which were deposited in non-marine, fluvial and lacustrine environments, with the most abundant coal seams found in the WCM[9].

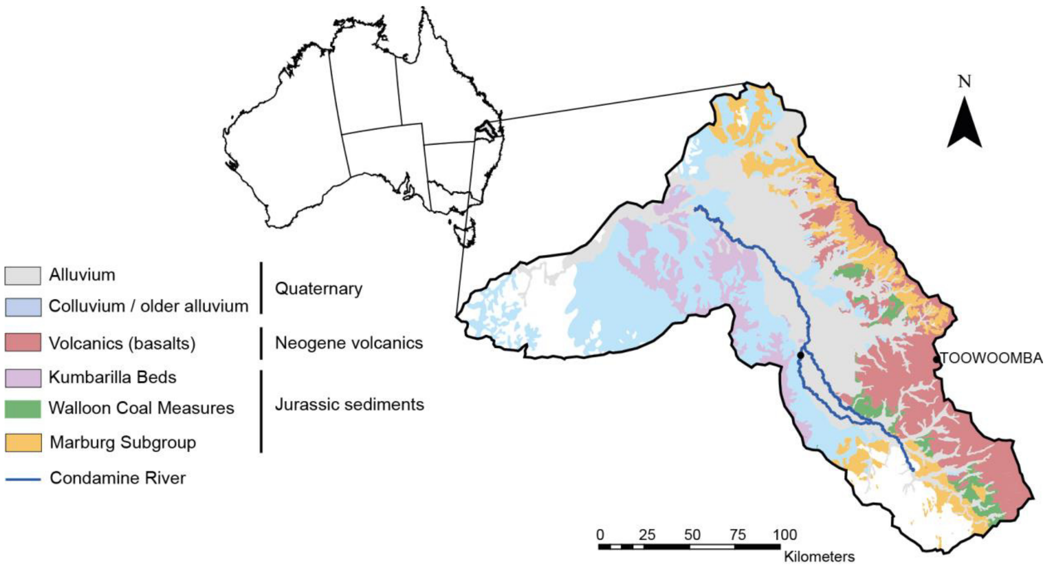

Figure 1. Upper Condamine catchment, Queensland, Australia. The Marburg Subgroup consists of: Gatton Sandstone and the Koukandowie Formation, herein undifferentiated. The Kumbarilla Beds consists of: Springbok Sandstone, Mooga Sandstone, Orallo Formation, Gubberamunda Sandstone and Bungil Formation, herein undifferentiated.

These sedimentary deposits dip to the southwest beneath the Condamine alluvium, and in some cases, the alluvium has incised the WCM by up to 130 m within a paleovalley[10]. Commercial quantities of predominantly biogenic methane gas occur in a shallow CSG reservoir of the Jurassic Walloon Coal Measures, but these concentrated gas reserves are significantly deeper (300m+).

2. Methods

Approximately 30 groundwater samples from alluvial, coal measures, shallow bedrock and basalt aquifers were collected for major, trace elements and lithium isotope analysis. The sampling strategy focused on potential areas of aquifer interaction between all aquifers as well as along the potential flow path within the coal measures as the feature dips to the south west. Groundwater samples were also taken from deeper areas of the coal measures, where coal and coal seam gas are prevalent. Basalt rock and coal samples were also taken and used in lithium isotope leaching experiments to obtain end member lithium isotopic values of coal and basalt minerals during leaching experiments.

Lithium isotopes were measured using the Neptune MC-ICP-MS at the Laboratory Division of the French Geological Survey (BRGM), Orléans, France. Standard sampling bracketing method and L-SVEC standard solution were used to determine δ^7Li values. Cationic resin (BioRad AG 50W-X12, 200-400 mesh) and 0.2N HCl acid media (for 30 ng of lithium) was used to achieve chemical separation of lithium. The method has a precision for δ^7Li determination of approximately 0.1-0.2‰.

3. Preliminary results

Relatively lower Li/Na ratios for alluvial water samples, when compared to basalt and coal measure water samples, reflects different weathering processes between the alluvium and adjacent aquifers. The incorporation of lithium into clay minerals and/or salinization likely to be driving lower Li/Na ratios in the alluvium (Figure 2a). Relatively high Li/Na ratios for one alluvial water sample were observed: this water sample occurs in a transition zone between the alluvium and underlying coal measures (Figure 2a).

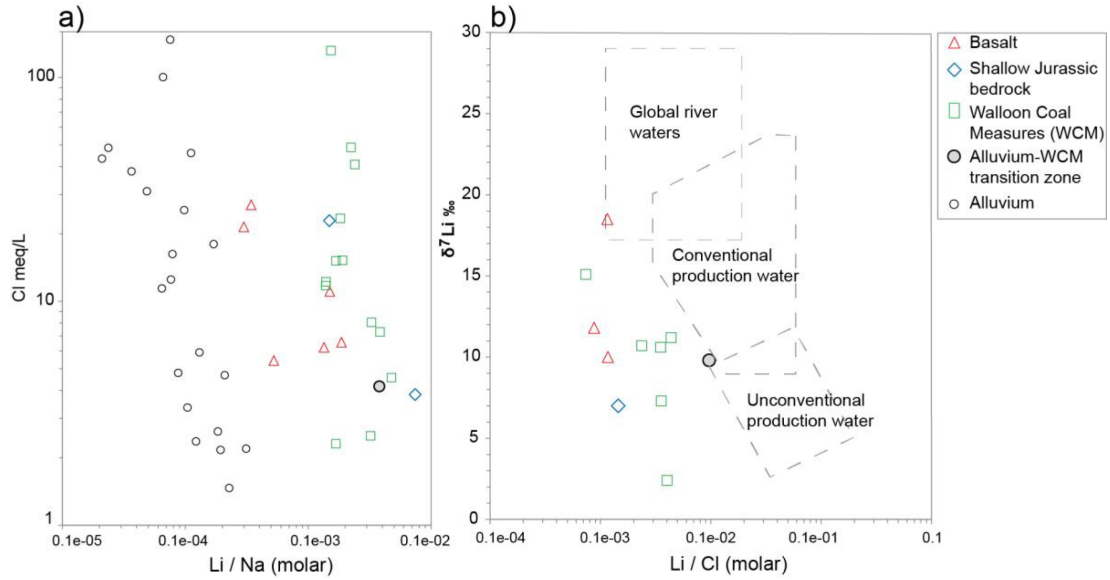

Figure 2 a) Li/Na versus chloride concentrations for alluvial, basalt, shallow sedimentary bedrock and coal measure aquifers; and b) Li/Cl versus δ^7Li for alluvial, basalt, shallow sedimentary bedrock and coal measure aquifers.

Preliminary results for lithium isotopes show varying δ^7Li values between basalt and coal measure water samples (Figure 2b). Generally, basalt water samples are more enriched in ^{7}Li than coal measure water samples. High and low δ^7Li values for coal measure water samples suggest different flow paths for this aquifer. The coal measures sample with high δ^7Li occurs in an area where basalt discharge and/or runoff from basalt outcrops is potentially recharging the alluvium and underlying coal measures. Interestingly the coal measure with lowest δ^7Li value occurs in an area where the coal measures outcrop and direct recharge is likely, with nearby basalt groundwater having much higher δ^7Li values (δ^7Li>18‰).

Water samples from coal measures that contained methane had δ^7Li values between 7 and 11‰. These samples can be expected to be influenced by coal and the early stages methanogenesis; they occur up-gradient of the deeper CSG reserves. No relationship between δ^7Li and methane concentrations or the $^{13}C\text{-}CH_4$ or ^{2}H-CH4 were observed. A water sample from the alluvium-coal measure transition zone is distinct from a coal measure water sample taken directly underlying the transition zone at a nested bore site (Figure 2b). The result suggests that the transition zone and coal measures are subject to independent influences and may have limited hydrologic connection. Further analyses will be performed for alluvial water samples to investigate relationships between the transition zone, coal measures and alluvium.

Further δ^7Li analyses will also be performed on groundwater samples from coal seam gas wells, where coal and methanogenesis are prevalent, as well as on leachate water from basalt and coal leaching experiments. The boundaries for conventional and unconventional production waters are shown on Figure 2 for reference. These reflect the weathering of shales and the possible transport of water from depth in marine settings associated with petroleum deposits[5,6]. The preliminary results shown here suggest the coal-bearing sedimentary feature (the Walloon Coal Measures) have distinct lithium isotope signatures, but no work has previously been done on the influence of coal on lithium isotopes: additional analyses will also be presented to compare δ^7Li of coal seams with other conventional and unconventional production waters.

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References

1. Tang, Y.-J., H.-F. Zhang, and J.-F. Ying, *Review of the Lithium Isotope System as a Geochemical Tracer.* International Geology Review, 2007. **49**(4): p. 374-388.
2. Négrel, P., R. Millot, C. Guerrot, E. Petelet-Giraud, A. Brenot, and E. Malcuit, *Heterogeneities and interconnections in groundwaters: Coupled B, Li and stable-isotope variations in a large aquifer system (Eocene Sand aquifer, Southwestern France).* Chemical Geology, 2012. **296-297**: p. 83-95.
3. Meredith, K., T. Moriguti, P. Tomascak, S. Hollins, and E. Nakamura, *The lithium, boron and strontium isotopic systematics of groundwaters from an arid aquifer system: Implications for recharge and weathering processes.* Geochimica et Cosmochimica Acta, 2013. **112**: p. 20-31.
4. Warner, N.R., T.H. Darrah, R.B. Jackson, R. Millot, W. Kloppmann, and A. Vengosh, *New Tracers Identify Hydraulic Fracturing Fluids and Accidental Releases from Oil and Gas Operations.* Environmental Science & Technology, 2014. **48**(21): p. 12552-12560.
5. Macpherson, G.L., R.C. Capo, B.W. Stewart, T.T. Phan, K. Schroeder, and R.W. Hammack, *Temperature-dependent Li isotope ratios in Appalachian Plateau and Gulf Coast Sedimentary Basin saline water.* Geofluids, 2014. **14**(4): p. 419-429.
6. Chan, L.-H., A. Starinsky, and A. Katz, *The behavior of lithium and its isotopes in oilfield brines: evidence from the Heletz-Kokhav field, Israel.* Geochimica et Cosmochimica Acta, 2002. **66**(4): p. 615-623.
7. Seredin, V.V., S. Dai, Y. Sun, and I.Y. Chekryzhov, *Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies.* Applied Geochemistry, 2013. **31**(0): p. 1-11.
8. Qin, S., C. Zhao, Y. Li, and Y. Zhang, *Review of coal as a promising source of lithium.* International Journal of Oil, Gas and Coal Technology, 2015. **9**(2): p. 215-229.
9. Exon, N.F., *The Geology of the Surat Basin: Bulletin 166*, in *Bureau of Mineral Resources, Geology and Geophysics*, D.o.N. Resources, Editor. 1976, Australian Government Publishing Service: Canberra, ACT. p. 230.
10. QWC, *Underground water impact report for the Surat Cumulative Management Area*, Q.W. Commission, Editor. 2012: Brisbane.