## Lithium isotope composition of lunar crust – Rapid crystallization and post-solidification quiescence?

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Lunar crust consists of ferroan anorthosites (~80%) and Mg-rich suite lithologies (~20%). It represents products from the most ancient lunar magmatic events (>4.1 Gyr [1]) and is accepted to have formed through plagioclase flotation on the lunar magma ocean (LMO) [2], from which significant amounts of incompatible elements (e.g. K, Th and U) were concentrated in the residual LMO melt (KREEP). Lithium has received little attention [3–6] despite its utility in tracking the history of the terrestrial crust [7–9].

New Li data show that anorthosites are the most Li-depleted lunar material known to date with <1 ppm in pristine samples. This is consistent with [6] and opposite to Earth's continental crust [7, 8] and may in part be explained by limited Li partitioning into plagioclase (K<sub>d</sub><sup>plg-melt</sup> ~0.2, [10]) from progressively crystallizing LMO for which ~3-4 ppm Li would thus be estimated. This appears higher than Li content of the Earth's mantle [3, 4]; the nature of such a difference is currently unclear but it could perhaps reflect a lack of net Li depletion before the accretion of the Moon [11]. Anorthosites show uniformly high  $\delta^7$ Li>5.7‰ (up to 9.4‰), distinct from mare basalts [3-5] as well as the Earth's continental crust [7, 8].  $\delta^7$ Li of norite 77215 with a KREEP affinity is resolved from other KREEP-rich lithologies [5]. The tight positive correlation of  $\delta^7$ Li with Na across the whole suite may reflect fractional crystallization of clinopyroxene appearing on the liquidus shortly after plagioclase during LMO crystallization. Overall, the Li data suggest (i) rapid plagioclase segregation without further re-equilibration with remaining LMO (through equilibrium Li isotope fractionation) and (ii) little subsequent modification of the lunar crust without an influence from younger magmatic events.

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Magna et al. (2009) GCA 73, A816. [6] Steele et al. (1980) LPSC XI, 571–590. [7] Teng et al. (2004) GCA 68, 4167–4178. [8] Magna et al. (2010) ChG 274, 94–107. [9] Ushikubo et al. (2008) EPSL 272, 666–676. [10] Bindeman et al. (1998) GCA 62, 1175–1193. [11] Magna et al. (2011) GCA 75, 2137–2158

## Surface and subsurface geochemical monitoring of an EOR-CO<sub>2</sub> field: Buracica, Brazil

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We present a surface and subsurface geochemical survey of the Buracica EOR-CO<sub>2</sub> field on-shore Brazil. A methodology coupling the stable isotopes of carbon with the noble gases was adopted to investigate the adequacy of a geochemical monitoring to track deep fluid leakage at the surface, with a scope of future application in the developping CCS industry. Three campaigns of CO<sub>2</sub> flux and concentration in soils were performed to understand the CO<sub>2</sub> variability across the field. The distribution of the CO<sub>2</sub> soil contents between 0.8 to 14 % is correlated with the proprieties of the soil, with a first order topographic control. These results, together with a  $\delta^{13}C_{CO2}$  between -15 and -23 ‰, suggest that the bulk of the soil CO<sub>2</sub> flux at Buracica is biological.

The gas injected and produced at numerous wells across the field showed a great spatial and somewhat temporal heterogeneity with respect to molecular,  $\delta^{13}C_{CO2}$  and noble gas compositions. The injected  $CO_2$  is characterized by  $\delta^{13}C_{CO2}$ near -31 ‰ and a peculiar noble gas composition enriched in Kr with respect to atmospheric values, while being depleted in the lighter noble gases. The heterogeneity of the gas produced from the reservoir is a consequence of the EOR-induced sweeping of the indigenous fluids by the injected CO<sub>2</sub>, producing a heterogeneous mixing controlled by 1) the production scheme and 2) the distribution in reservoir permeability. In the light of the  $\delta^{13}C_{CO2}$  found in the reservoir (from -36 to +6 ‰), the stable isotopic composition of carbon revealed insufficient to track CO2 leaks at the surface. We demonstrate how noble gases may be powerful leak discriminators, even for CO2 abundances in soils in the bottom range of the biological baseline (~1 %). The results presented in this study show the potentiality of geochemical monitoring techniques, involving stable isotopes and noble gases at the reservoir and soil levels, for tracing CO2 in CCS and EOR projects.

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