

Semantimetasomatism

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“When I use a word,” Humpty Dumpty said, “it means just what I choose it to mean ...” Many geochemists use “metasomatism” in this way. Like dark energy and magic, the main evidence in support of trace element metasomatism is often that data don’t conform to quantitative theory. In this talk I will expand on why this can be a problem, and suggest partial solutions.

“Metasomatism” refers to geochemical fractionation resulting from open-system interactions between a moving fluid or melt and an assemblage of minerals. Metasomatic processes involve *input* of fluid or melt, with or without output. They include hydrothermal alteration, flux melting, impregnation, assimilation, zone refining and chromatography. What is gained by calling all “metasomatic”? And, “equilibrium porous flow” (metasomatism) can be chemically identical to batch melting (not metasomatism). Similarly, melt extraction followed by “metasomatic enrichment” can look just like flux melting, Fluid fluxed, or melt fluxed? Supercritical goo? Who cares?

We can parse metasomatism into clearly defined processes. However, while causality may be clear in numerical or experimental models, “similarity” between rock data and models may not be unique. Many high temperature processes closely approximate grain scale equilibrium, but this is coupled with fractional distillation or other kinetic effects on a larger scale. Equilibrium is path independent and reversible, but disequilibrium is not. We can document “reaction progress” in the field or within samples, finding correlated chemical and spatial data. This reduces the number of models consistent with data. We can conceptually discriminate between processes in which fluid or melt mass increases, is constant, or decreases. Local effects may be identical, but their progressive evolution in time and space should be distinct. Multi-scale spatial studies will be increasingly valuable in studying melt transport in the mantle, for example.

Metasomatism above subduction zones is crucial for global geochemical cycles. Despite the recognition of supercritical melts in subduction zone conditions, we can document the “direction” of mass transfer in high P and UHP terranes, and interpret data within theoretical bounds defined by dilute aqueous fluids versus hydrous melts, just as we use fictive end-members, batch and fractional melting, as benchmarks in studying residual peridotites.

In summary, spatial studies will relate metasomatism to the geotherm, geochemical cycling, and geodynamics.

Regionally extensive light lithium in mantle lithosphere of far east Russia

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Lithium isotopes are increasingly employed to understand crustal recycling within the Earth, but the composition of lithium recycled from crust to mantle is uncertain. Because altered oceanic crust takes up isotopically heavy lithium from sea water, the subducted slab is generally expected to deliver heavy lithium to the mantle, yet, eclogites, considered analogs to subducted oceanic crust, have $\delta^7\text{Li}$ values that are generally lighter than MORB (down to -12‰). These light values may reflect loss of heavy lithium via low-T dehydration reactions in the down-going slab (Zack et al., 2003). Recently, Nishio et al. (2004) reported unusually low $\delta^7\text{Li}$ values for clinopyroxenes from mantle xenoliths from far east Russia and southern Japan. They interpreted these light values to reflect influx of lithium from a subducted slab and argued that acid leaching, applied to all samples, did not affect the lithium isotopic composition of the cpx. We have analysed cpx separates from well-characterized peridotite xenoliths from Far East Russia: six from the Tok volcanic field (400-1000 km to the north of the sites sampled by Nishio et al.) and one from the Barhatny volcano (near the Ennokentiev site of Nishio et al.). The xenoliths range from fertile to highly refractory in terms of modal and major element compositions (1.1 to 4 wt.% Al_2O_3), reflecting variable amounts of melt extraction at shallow levels (Ionov et al., 2005). All the xenoliths are metasomatized to various degrees (e.g., most are LREE-enriched). The cpx have variable, but mainly high lithium contents (ranging up to 16 ppm), and all show unusually light $\delta^7\text{Li}$ values (-6 to -14‰), irrespective of whether the minerals were mildly acid leached or simply washed in milli-Q water. Moreover, the enrichments in lithium and the low $\delta^7\text{Li}$ values do not appear to be correlated with Al contents, enrichments in highly incompatible trace elements or Sr and Nd isotope compositions. Although we cannot directly link the metasomatism of these samples with modern or ancient subduction zone fluids, a region of unusually low $\delta^7\text{Li}$ exists within the lithospheric mantle, stretching for over 1000 km, adjacent to the Pacific rim.

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Relics of subcontinental mantle in the Cape Verde oceanic lithosphere

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Mantle xenoliths from two Late Tertiary necks of Sal Island were investigated in order to define the petrological characteristics together with the compositional evolution of the Atlantic lithospheric mantle underneath Cape Verde Archipelago. They consist of mainly protogranular sp-bearing lherzolites and harzburgites. Whole rock and pyroxene trace element distribution, particularly HREE, suggest that compositional variation from lherzolites to harzburgites cannot be explained by a common progressive depletion process of a sp-bearing mantle peridotite. High Cr₂O₃, low CaO contents and upward-convex REE patterns in large protogranular clinopyroxenes ($La_N=3.6-5.3$; $Sm_N=8.3-12.8$; $Yb_N=2.4-4.8$), coupled with high Cr₂O₃ and low HREE contents in orthopyroxene, suggest in fact that lherzolites still preserve geochemical fingerprints consistent with a fertile gt-bearing stability field. By contrast the majority of Cape Verde harzburgites, are quite comparable to highly refractory mantle lithologies commonly observed in the Atlantic Ocean generated after extensive MORB extraction. This is also in agreement with the occurrence of Late Jurassic MORB in the islands of Maio and Santiago. On the other hand the abundant presence of lherzolites-still recording equilibration in the garnet stability field-suggests that a significant portion of Cape Verde lithospheric mantle was not formed at mid-ocean ridge, but most probably represent a portion of sublithospheric continental mantle incorporated in the newly-formed oceanic lithosphere. A few lherzolites and harzburgites show textural evidences of metasomatic enrichments. Metasomatic fluids react with the original paragenesis causing the formation of secondary minerals, such as clinopyroxenes after orthopyroxene and primary clinopyroxene destabilization and, in few cases, k-feldspar and K₂O-rich glass (K₂O up to 8.78wt%). These agents were reconstructed using major and trace element mass balance calculations between primary and secondary parageneses. The resulting compositions have geochemical features comparable to those of kimberlite (on dry basis, MgO:17-27 wt%; K₂O/Na₂O:1.6-3.2 molar; (K₂O+Na₂O)/Al₂O₃:1.1-3.0 molar; Rb:91-165 ppm; Zr:194-238ppm). These magmas may result from very low partial melting degree of deeper SCLM portions, left behind by drifting of the African Plate during the Central Atlantic opening.

Fluid-rock interaction in convergent margins: Evidence from stable isotopic studies of veins

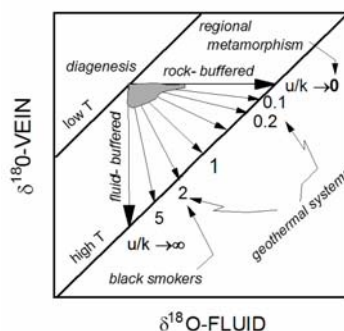
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Measurements of the oxygen isotope ratios of veins and their coexisting host rocks from the Lachlan Fold Belt (Australia), the Ouachita and Appalachian Orogens (United States), the Otago Schist (New Zealand) and the Oman Mountains constrain the styles of fluid-rock interaction in the crust at different levels during crustal convergence. The ratio of the fluid flux rate (u) to the isotopic exchange rate (k) is the dominant parameter effecting oxygen isotope distribution.

Modeling of the isotopic exchange shows that for many geologic environments the isotopic composition of the fluid reaches a quasi-steady state that can be approximated by a mixing equation of a rock-buffered fluid ($u/k \rightarrow 0$) and an externally derived fluid ($u/k \rightarrow \infty$); in a fluid + rock binary



system, any natural system generates a spectrum of fluid compositions that range from fluid-buffered to rock-buffered. The primary controls on this critical u/k ratio are permeability (for u) and temperature (for k). Mechanical limits

on permeability at depth permit the preservation of surface-derived isotopic heterogeneities to significant depths and for geologically extensive time scales. When $u/k \ll 1$, the fluid isotopic composition is buffered by the local host rocks on time scales of thousands of years while mineral heterogeneities will persist for millions of years. Secondary phases grown in the presence of this rock-buffered fluid will reflect isotopic equilibrium with the local fluid environment and exhibit non-equilibrium fractionations with the remaining partially-exchanged phases. The time scales for this style of fluid-rock interaction are comparable to the time scales for metamorphism in convergent margin settings.

Jadeitite: A record of metasomatism at various depths in Guatemalan subduction zones

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Jadeitites crystallize from hydrous subduction-related fluids in serpentinizing peridotite. The strike-slip Motagua Fault in Guatemala has brought jadeitites to the surface several times. Along the north side of that fault we studied 8 jadeitite locales along 65 km of E-W strike, and on the south side 3 locales along 15 km. We identified at least 4 distinct PTx settings for jadeitite.

Jadeitites north of the fault are all quite similar, light colored and altered by late-stage fluids. The presence or absence of potassic phases may be a further subdivision. A modest jadeite (Jd) – omphacite (Omph) gap and zoisite suggest 300-400°C. Absence of quartz (Qtz) and common albite (Ab), mica, and late analcime (Anl) suggests P = 6-10 kb. Albitites are common, implying further fluid crystallization at lower P and higher a_{SiO_2} . The associated rocks are garnet-zoisite-amphibole (with some retrograde eclogite) and omphacite-taramite metabasites. The southern jadeitites are subdivided as follows:

1- San Jose jadeitites are green to blue-green with late omphacite veins and little alteration. A larger Jd – Omph gap and lawsonite suggest 300-400°C, and higher P as indicated by Qtz at P = 12-20 kb. Lawsonite eclogites (P = 20-25 kbar, T = 350-450°C) occur with these jadeitites.

2- La Ceiba jadeitites are moderate to intense dark green, occasionally lavender, with veins of quartz, diopside, cymrite, and vesuvianite. A large Jd – Omph gap suggests 300-400°C and, as indicated by Qtz ± Ab, P = 10-14 kb. These coexist with omphacite-glaucophane blueschists.

3- La Ensenada jadeitites are whitish with green, blue, orange, and mauve. A large Jd – Omph gap and pumpellyite suggests <200~300°C at lower P=6-9 kb as indicated by primary Ab and secondary Anl. These are very low in iron and coexist with pure clinocllore and magnetite, which all suggest ferrous iron removal by a fluid. These are found with lawsonite-glaucophane blueschists and chloritite.

These four types of Guatemalan jadeitite record differences in fluid composition, crystallization T and P, and a variety of sodic metasomatic processes.

The origin of replacement dolomite, Dolomites, northern Italy: Part 1

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Massive dolomite typically forms at depth and elevated T through replacement of limestone by its reaction with flowing dolomitizing fluid. Details of the physical mechanisms of flow, and the chemical reactions remain unresolved. Our integrated mapping, stable isotope, and major- and trace-element study of the Triassic Latemar buildup addresses these issues. The Latemar is an ideal study area because dolomitization was arrested with both dolomite and unreacted limestone well-exposed in 3D. Boundaries between the dolomitized and undolomitized regions are sharp (usually <10 cm wide) and are easily mapped because of a color difference between limestone and dolomite. The distribution of dolomite was mapped on buildup- to m-scales to define the flow channels of dolomitizing fluid. Dolomite at lower elevations occurs as brecciated columns or vertical sheets; at higher elevations dolomite occurs mainly as horizontal, bedding-parallel sheets and tubes, and less commonly as vertical breccia pipes and sheets parallel to fractures and margins of dikes. The distribution of dolomite images an orthogonal lattice of interconnected vertical and bedding-parallel flow channels. The $^{87}\text{Sr}/^{86}\text{Sr}$ of Latemar dolomite is 0.7076-0.7079 and fluid inclusions in dolomite have salinities 3.6-5.1 wt % NaCl equivalent [1], implying seawater or seawater-derived fluid was the agent of dolomitization. Dolomite has $\delta^{18}\text{O} = 21.5\text{-}27.4\text{‰}$ (VSMOW), corresponding to T = 52-88°C (assuming equilibration with fluid of $\delta^{18}\text{O} = 0$). Calcite in limestone has $\delta^{18}\text{O} = 23.3\text{-}28.4\text{‰}$, corresponding to T = 25-52°C. Dolomite has $\delta^{13}\text{C} = +1.9$ to $+4.4\text{‰}$ (VPDB), and calcite has $\delta^{13}\text{C} = +1.1$ to $+4.0\text{‰}$. Calcite in limestones has average $X_{\text{Ca}} = 0.987$, $X_{\text{Mg}} = 0.013$, and $X_{\text{Fe}} < 0.001$ (microprobe analysis). Typical dolomite has $X_{\text{Ca}} = 0.537$, $X_{\text{Mg}} = 0.457$, and $X_{\text{Fe}} = 0.006$, although dolomite that occurs in high-T regions is more enriched in Fe: $X_{\text{Ca}} = 0.520$, $X_{\text{Mg}} = 0.464$, and $X_{\text{Fe}} = 0.016$. The presence of Fe in dolomite, as well as Mn- and Zn-enrichment from preliminary LA-ICPMS data, indicates that Triassic seawater alone was not the dolomitizing fluid. We suggest a mixture of Triassic seawater and hydrothermal fluid produced by the reaction of seawater with hot, mafic rocks of the adjacent Predazzo volcanic-intrusive complex that was active during dolomitization.

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The origin of replacement dolomite, Dolomites, northern Italy: Part 2

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Analysis of the spatial distribution of elements, isotopes, and heat with transport theory leads to insights into the flow system that produced dolomite (Dol) in the Latemar buildup. From Part 1, Dol typically replaced calcite (Cal) in limestone by $2\text{Cal} + 0.89\text{Mg}^{2+} + 0.01\text{Fe}^{2+} = \text{Dol} + 0.90\text{Ca}^{2+}$. Constraints (Part 1) of a dolomitizing fluid with seawater-like salinity, $\text{Ca}/\text{Mg} < 0.75$ (for dolomitization at $\approx 75^\circ\text{C}$), and significant Fe, Mn, and Zn point to fluid similar in chemistry and T to modern diffuse effluent. The development of Dol over a distance ≈ 1 km along the inferred flow path then requires, by mass balance of Ca and Mg, a time-integrated fluid flux (q) $\approx 10^8 \text{ cm}^3 \text{ fluid}/\text{cm}^2 \text{ rock}$. Given the composition and amount of fluid, spatial distributions of isotope compositions were computed from the advection-diffusion equation. Carbonate rock is predicted to have equilibrated with respect to ^{18}O - ^{16}O , ^{87}Sr - ^{86}Sr , and ^{13}C - ^{12}C exchange with dolomitizing fluid over distances 850x, 24x, and 0.11x the extent of dolomitization along the flow path. Near Dol-limestone interfaces, $\delta^{13}\text{C}_{\text{Dol}}$ thus is simply inherited from the limestone parent (confirmed by data in Part 1) while $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Dol}}$ and $\delta^{18}\text{O}_{\text{Dol}}$ correspond to equilibration with the dolomitizing fluid. Measured $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Dol}}$ is evidence for a Middle Triassic seawater-derived fluid and $\delta^{18}\text{O}_{\text{Dol}}$ records the T of dolomitization (Part 1). The elevated T recorded by $\delta^{18}\text{O}_{\text{Cal}}$ (Part 1), indicates that physical limits of the flow channels extended into limestone adjacent to Dol and that flow in the limestone occurred at lower T. Ranges in $\delta^{18}\text{O}_{\text{Dol}}$ within individual outcrops almost as large as for all analyzed samples is qualitative evidence that fluid flow occurred in multiple pulses of limited spatial extent and at variable T. Profiles in $\delta^{18}\text{O}_{\text{Dol}}$ across some vertical flow channels record steep gradients in $T \approx 10\text{-}25^\circ\text{C}/\text{m}$. Quantitative analysis of the T profiles with the heat equation suggests that individual flow pulses had $q \approx 2 \cdot 10^5 \text{ cm}^3/\text{cm}^2$ and a duration of ≈ 0.5 y. Dolomitization in the area was accomplished by ≈ 500 flow pulses over a total duration of flow and reaction only ≈ 300 y. The occurrence of 10-15% porosity in many Dol samples confirms that most (but not all) Dol replaced Cal at constant C rather than at constant volume. Replacement at constant volume does not make geochemical sense because even $q \approx 10^8 \text{ cm}^3 \text{ fluid}/\text{cm}^2 \text{ rock}$ is inadequate to transport the necessary amount of dissolved C.

Geochemistry, mineralogy, and chronology of K-metasomatism of volcanic rocks near Socorro, New Mexico, USA

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Potassium metasomatism, thought to be caused by deep circulation of alkaline-saline brines, affects an area of roughly 1000 km² near Socorro, New Mexico, increasing the K₂O content of local volcanic rocks by up to 10 wt.%. Petrographic and microbeam analyses indicate that during the chemical changes associated with metasomatism, Na-rich phases, primarily plagioclase, are dissolved and replaced by secondary mineral phases, mainly adularia and clay minerals. Bulk geochemical analyses of altered rocks compared to fresh rocks demonstrate consistent chemical patterns, including enrichments of K₂O, Fe₂O₃, As, Rb, Pb, Sb, Ba, and Cs and depletions of MgO, CaO, Na₂O, Eu and Sr. Analyses of alteration phases hand-picked from relict plagioclase grains provide the clearest picture of the chemical processes that occur during alteration, and allow quantitative correlations between the presence of alteration phases and the abundance of elements such as K₂O, Rb, CaO, Na₂O, Eu and Sr. This analysis also suggests that variations of elements such as As, Pb, Sb, Ba, and Cs are related to hydrothermal alteration, either overprinting, or overprinted by, potassic metasomatism. A final chemical signature observed in hand-picked alteration mineral suites is that the REE content of samples from a low-REE rock unit increase during metasomatism, whereas there is a significant decrease in samples from a unit with higher initial REE contents, suggesting that the variation in REE contents may be related to equilibration between the rocks and the metasomatizing fluid. Results suggest that the enrichment of REE may be roughly related to the abundance of metasomatism-derived clay minerals in the sample.

The chronology of metasomatism determined by ⁴⁰Ar/³⁹Ar analysis of hand-picked secondary potassium feldspar, indicates that metasomatic alteration began at around 15 Ma, and continued to around 7 Ma. The areas that show the most intense effects of alteration yield the youngest ages, suggesting that this may represent the deepest, most central and longest-lived part of the playa system. The age range determined here is consistent with inferred timing of playa deposition from independent geological evidence.

The behavior of chlorine and $\delta^{37}\text{Cl}$ during the oceanic crust alteration

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The oceanic crust (OC) is a vector of chemical exchanges between the surface and the Earth's interior. Hydrothermal circulation in the ocean's floor is the major control of chemical compositions of both seawater (SW) derived fluids and crust (before subduction). In order to bring new constraints on the OC alteration, chlorine stable isotope composition ($\delta^{37}\text{Cl}$) was determined in both high (HTF) and low (LTF) temperature fluids, at ridge axis and off-axis, respectively, and in fresh and altered basalts.

Worldwide HTF ($T > 230^\circ\text{C}$) have a large range of chlorinity (250 to 821 mM), but show very constant $\delta^{37}\text{Cl}$, indistinguishable from the SW $\delta^{37}\text{Cl}$ (0.0‰). This $\delta^{37}\text{Cl}$ homogeneity suggests that the phase separation process, responsible for chlorinity variation at HT, does not fractionate Cl isotopes [1]. In contrast, despite very small variations of chlorinity (550± 6mM), LTF ($T \leq 60^\circ\text{C}$) show $\delta^{37}\text{Cl} = -0.71 \pm 0.67\text{‰}$ (1σ). Moreover, $\delta^{37}\text{Cl}$ values show positive covariations with $\delta^{18}\text{O}$ (mainly modified by water-rock interactions) suggesting that a single process leads to a depletion in ^{37}Cl of the interacting fluids.

Basalts, both fresh and altered at LT, are also depleted in ^{37}Cl relative to SW ($-2.0 < \delta^{37}\text{Cl} < -0.2\text{‰}$ and $-2.8 < \delta^{37}\text{Cl} < -0.5\text{‰}$, respectively). Cl of the reacting fluids has precipitated in the pores of the altered basalts upon drying. It was recovered by leaching as described in [2]. These residual salts, representative of the reacting fluids ($-5.1 < \delta^{37}\text{Cl} < 0.0\text{‰}$), have higher $\delta^{37}\text{Cl}$ than the associated whole rock, implying that $\Delta^{37}\text{Cl}_{\text{R-F}} < 0$. This contrasts with prior assumptions [3-4], and with classical fractionation laws predicting a ^{37}Cl enrichment of the solid phase.

Interaction of SW ($\delta^{37}\text{Cl} = 0\text{‰}$) with fresh OC ($\delta^{37}\text{Cl} < 0\text{‰}$) produces fluids and rocks with $\delta^{37}\text{Cl} \leq 0\text{‰}$. These data expose a mass balance problem.

References

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The metasomatic history of the lithospheric mantle beneath NE Spain

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The spinel peridotite suite at Olot, is remarkably bi-modal consisting of very fertile protogranular lherzolites, sometimes bearing texturally equilibrated pargasite amphibole (3 samples out of 60), and very refractory harzburgites showing secondary recrystallization textures. Bulk rock REE systematics are widely variable: lherzolites display flat or depleted LREE patterns (HREE concentration up to 2.7*Ch; La_N/Yb_N down to 0.42); harzburgites are extremely depleted in HREE (down to 0.21*Ch) displaying at the same time high LREE/HREE ratios ($\text{La}_N/\text{Yb}_N=12.3-17.2$); this LREE enrichment is coupled with relative enrichment in Th, U, Nb and Ta. In situ LA-ICP-MS analysis of clinopyroxene highlights LREE depleted compositions with a slight spike at Eu in anhydrous lherzolites (HREE up to 13*Ch, La_N/Yb_N down to 0.3, and $\text{Eu}^*=1.2-1.5$); the presence of LREE depletion (La_N/Yb_N down to 0.2) coupled with a Eu positive anomaly (Eu^* up to 1.7) also characterize the clinopyroxenes of two amph-bearing lherzolites. In these samples the clinopyroxene composition mimics, at slightly lower concentration, that of the coexisting amphiboles. The constituent clinopyroxenes of harzburgites display totally different REE distributions, characterised by remarkable HREE depletion (down to 0.4*Ch) and ubiquitous M/LREE enrichment. In these harzburgites, Nd_N/Yb_N (up to 20.7*Ch) is generally higher than La_N/Yb_N (up to 12*Ch) giving rise to upward convex patterns. Geochemical features of the harzburgites indicate that the mantle section sampled beneath this area suffered major episodes of melt extraction followed by metasomatic processes - triggered by highly alkaline melts - that induced cryptic enrichments. Lherzolites, on the other hand, possibly indicate modal re-fertilization by pervasive impregnation of subalkaline (LREE-depleted) melts.

Metasomatic processes of Paleozoic lithospheric mantle of Scotland Terranes

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Mantle melting events occurring intermittently from the late Carboniferous to mid-Permian in northern and north-western Scotland relate to lithospheric extension, generated small volumes of silica-deficient basic magmas, which in some cases, contain peridotitic xenoliths. The present work concerns mantle peridotites from several localities of the Northern Highlands Terrane (Rinibar, Orkney- and Streap Com'laidh) of Midland Valley Terrane (Rudduns Point). A comparison with rare peridotite xenoliths from Hebridean Terrane, Grampian Highland Terrane and Southern Uplands Terrane which also experienced variable metasomatic enrichment is also put forward, with the aim of studying the evolutionary history of Scottish lithospheric mantle and highlighting the metasomatic agents which affected this portion of mantle during Paleozoic. Attention was mainly focussed on major and trace element contents of minerals, namely clinopyroxenes. In the Northern Highland Terrane, clinopyroxenes from Streap Com'laidh are less LREE-enriched and present less pronounced Ti and Zr anomalies (La/YbN 2.8-4.5; Zr* 0.42-0.57; Ti* 0.57-0.62) than clinopyroxenes from Rinibar. Clinopyroxenes from Rinibar have been variably enriched in LREE, with La/YbN ratios ranging from 2.7 to 32.2. Remarkable Ti and Zr negative anomalies, although to variable extent, are noticed (Zr* 0.10 - 0.86; Ti* 0.07 - 0.28). Phlogopite is present, and can account for the pronounced Ti negative anomaly in some clinopyroxenes. Two different enrichment styles can be identified in the Orkney's lithospheric mantle: one presenting LREE-enrichment and remarkable Zr (and Hf) and Ti negative anomalies, the other with LREE-depletion (compared to MREE) and less pronounced Ti (and Zr) negative anomalies, associated with the presence of high-TiO₂ phlogopite. The two kinds of clinopyroxenes compare well with clinopyroxenes related to carbonatite and kimberlite metasomatism respectively. A progressive enrichment process may also be envisaged between clinopyroxenes in xenoliths from Midland Valley Terrane, and those from Hebridean Craton.

REE distribution in granites from the Crown Jewel gold skarn deposit: A LA-ICP-MS study

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Garnets from the Crown Jewel Au-skarn deposit, north-central Washington, range in composition from Adr₃₀Gr₇₀ to almost pure andradite (Adr_{>99}). Fe-rich garnets are isotropic whereas Al-rich garnets significantly deviate from cubic symmetry and are anisotropic, often showing sectorial dodecahedral twinning.

In situ LA-ICP-MS analyses of those garnets reveal a positive correlation of ΣREE^{3+} (<1-47 ppm) with Al content (0-2.6 a.p.u.f.), and consequently with their grossular component. REE patterns for Al-rich garnets show HREE-enrichment and LREE-depletion, and weak positive and negative Eu anomalies. Fe-rich garnets (Adr_{>90}) have much lower ΣREE and exhibit LREE-enriched and HREE-depleted patterns, with a strong positive Eu anomaly. Presence of magnetite, implying a reduced environment with $f\text{O}_2$ below the HM buffer, indicates that Eu is present as Eu²⁺, which in part explains its different behaviour from the other REEs and the consequent Eu/Eu* anomalies. Incorporation of REE into garnet is partially controlled by its crystal chemistry. REE³⁺ follow a coupled, YAG-type substitution mechanism ($[\text{X}^{2+}]_{-1}^{\text{VIII}}[\text{REE}^{3+}]_{+1}^{\text{VIII}}[\text{Si}^{4+}]_{-1}^{\text{IV}}[\text{Z}^{3+}]_{+1}^{\text{IV}}$), while Eu²⁺ substitutes for X²⁺ cations. Thermodynamic data (e.g., Hmixture) suggests preferential incorporation of HREE in grossular and LREE in andradite.

Textural evidence, optical characteristics and major and trace element geochemistry, show that variations observed in the Crown Jewel garnets are largely controlled by external factors (fluid composition, W/R ratios, mineral growth kinetics, and diffusive vs. advective metasomatism). The data are consistent with Al-rich garnets being formed by diffusive metasomatism, under low W/R ratios, and in equilibrium with metasomatic fluids whose composition is locally buffered by the host rocks. On the other hand, Fe-rich garnets grow rapidly by advective metasomatism, under relatively high W/R ratios, and in equilibrium with a magmatic-derived fluid, consistent with an increase in porosity by fracturing.

Geochemistry and petrogenesis of a South African diamondiferous eclogite

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A recently collected diamond-bearing eclogite from the Roberts Victor Mine of South Africa was studied for its major and trace element chemistry and mineral compositions, to gain insight into the relationships between eclogite and diamond petrogenesis. The relatively magnesian basaltic bulk composition of this xenolith is characteristic of other Roberts Victor eclogites. Its high Na₂O in garnet and K₂O in clinopyroxene puts this eclogite in the Group I classification group of McCandless and Gurney (1989), in common with most diamondiferous eclogites. Garnet-clinopyroxene Fe-Mg exchange thermometry yields an estimate of 1114°C at 30 kbars, also similar to estimates from other Roberts Victor Group I eclogites.

However, in contrast to most Group I eclogites, the reconstructed bulk rock rare earth element pattern of this rock (determined by ion probe analysis of unaltered garnet and clinopyroxene) is light rare earth depleted, with a positive europium anomaly, indicative of a plagioclase-rich cumulate gabbroic protolith metamorphosed to eclogite facies during emplacement into the lithosphere. In this regard, and in its textural character, (MacGregor and Manton, 1986) the xenolith is more similar to Group II eclogites. This contrast in classification may point to diamond growth during metasomatic reenrichment of an originally depleted cumulate rock matrix, and emphasizes the diversity of protoliths in which diamonds may form through metasomatic processes.

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Tracing metasomatic agents by noble gas isotopes

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Elemental and isotopic compositions of noble gases trapped in ultramafic rocks provide valuable information regarding the processes that affected the terrestrial mantle. Here I present some of such examples we found in fresh suites of xenoliths from SE Australia (e.g., Matsumoto et al., 2000) and in orogenic peridotites from Horoman (Matsumoto et al., 2001) and from Finero complexes (Matsumoto et al., 2005, submitted) with a particular emphasis on mantle metasomatism.

Based on analyses on above mentioned suites of rocks, we identified at least four kinds of characteristic noble gas components:

- (1) A MORB-type isotopic component
- (2) A Plume-like component
- (3) A hybrid component with mantle-He and air-Ar
- (4) A highly radiogenic component

Irrespective of their isotope signatures, these components are preserved in fluid inclusions without being significantly disturbed by ingrowths of radio- and nucleogenic noble gas isotopes. Therefore, these noble gas signatures should reflect those of mantle domains from which respective metasomatic agents had been derived. A MORB-like component is the most widespread in variably metasomatized mantle xenoliths from SE Australia, whereas the plume-like neon is rare and only found in metasomatic apatite, indicating an involvement of mantle plume to this particular metasomatic event (e.g., Matsumoto et al., 1997 and 2004). A Hybrid of mantle-He and air-Ar can be regarded as a signature characteristic of the subduction zone settings, and is often found in orogenic lherzolites. We also found that this component is highly concentrated in thin apatite-rich layer of Finero lherzolite that hosts LREE-enrichment. This can be taken as rather direct evidence for metasomatic introduction of incompatible elements and noble gases with the same agent. Also, it is possible identify more than two different noble gas components coexist in a single specimen, suggesting multiple episodes of metasomatism. These demonstrate the usefulness of noble gas isotopes to constrain tectonic setting of the metasomatism and source of its agent.

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Effects of K-metasomatism on the REE compositions of Precambrian Aravalli paleosols, Northwestern India

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Metamorphosed and metasomatized Precambrian paleosols occur at the base of the Paleoproterozoic Aravalli Supergroup, NW India. These paleosols have developed on granitic, gneissic and amphibolitic parent rocks constituting the 3.3 to 2.5 Ga basement gneissic complex. The paleosols have probably developed between 2.5 and 2.2 Ga. Based on detailed studies, it has been proposed that these rocks have witnessed a complex evolutionary history of metamorphism followed by metasomatism [1].

Rb-Sr isotopic analysis on wholerock and mineral separate samples have been carried out to delineate the timing of alkali metasomatism and to assess its effects on rare earth element (REE) and Th, U elemental compositions. The Rb-Sr isotopic data of paleosol samples yielded an age of 1399 ± 26 Ma with a very high Sr_i of 0.75145 ± 0.00063 . The $^{87}Sr/^{86}Sr$ data show a good correlation with $1/Sr$ values indicating that the observed straight line between Rb-Sr isotope compositions may be a result of mixing. However, the overlying metasomatically altered basaltic rocks also yielded Rb-Sr age of 1397 ± 53 Ma, indicating that the age obtained on paleosols may represent the timing of alkali metasomatism. Several Precambrian paleosols have also yielded Rb-Sr ages younger than their stratigraphic ages emphasizing the usefulness of paleosols as indicators of timing of alkali metasomatism [2].

Importantly, it has been noticed that Th, U and REE contents of the Aravalli paleosols are correlated with $^{87}Sr/^{86}Sr$ ratios indicating that they might have mobilized during alkali metasomatism. However, the Ce and Eu anomalies, which are more important for assessing the redox state of the Precambrian atmosphere appears to have been not correlated with the Sr isotope ratios.

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A synthesis of diamond and inclusion trace element studies

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We have performed in-situ trace element analysis of inclusions in diamond and of their diamond host by Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS). Impurities in the diamond host are attributed to sub-microscopic quenched melt inclusions which represent a metasomatic melt or a melt produced during mantle metasomatism. The trace element compositions of inclusions often indicate complex histories, this is difficult to reconcile with a syngenetic origin for diamond inclusions; therefore several workers prefer protogenetic growth.

We use partition coefficients to calculate the composition of melt in equilibrium with the crystalline inclusions and compare this to the analysed melt composition. If the inclusions are syngenetic, then the calculated and measured melt composition should lie along a fractionation trend. If the inclusions are protogenetic, then the diamond growth event will be one of a number of geochemical events affecting the included mineral. In either case, this data provides important information about the diamond growth event.

Traverses are used to look for distinct geochemical events and fractionation trends during diamond growth, with reference to the lattice-bound nitrogen concentration and aggregation state. This work forms a link between established inclusion studies and exciting new data from LA-ICP-MS fingerprinting of diamonds by provenance and paragenesis.

The behavior of boron in hydrothermal alterations of granites

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Boron contents and B-isotopic compositions are measured on fresh and altered granite samples from the Qitianling granite and related hydrothermal tin deposit in South China. The fresh granite has the highest boron content (36.62ppm) and the highest $\delta^{11}\text{B}$ value (-10.9‰). The granites near the tin ore veins were slightly altered and have lower boron contents (12.12 to 24.77ppm) and lower isotopic compositions (-15.6 to -13.4‰). The completely chloritized granites sampled from the tin veins have the lowest boron isotopic compositions (-27.3 to -21.9‰). B/Be and $\delta^{11}\text{B}$ values of granites decrease with increasing degrees of hydrothermal alteration. Boron isotopic variations are consistent with those of oxygen isotopes. The fresh granites have the highest oxygen isotopic composition ($\delta^{18}\text{O}=10.5\text{‰}$). The most altered granites have the lowest oxygen isotopic composition (5.4 to 6.6‰). The oxygen isotopic variations of granites are the result of fluid-rock interactions. The colinearity of isotope ratios of B and O of granites indicated that the fractionation of boron isotope is also the result of fluid-rock interactions. These data indicate that the heavier isotope, ^{11}B is preferentially lost to hydrous fluids from altered granites during the fluid-rock interactions. It may be explained by coordination-dependent fractionation of trace B between tetrahedral sites in silicate and trigonal sites in hydrothermal fluids. This study identifies for the first time that boron isotope is an excellent tracer for hydrothermal alterations of granites and may be used as a useful exploration guide for mineralization. Future studies of the boron isotopic fractionations between main rock-forming minerals and hydrothermal fluids are needed in order to understand this tracer better.

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