

EUG XI



Symposium MS10

The Role of Mantle Carbon in the
Global Carbon Cycle
(A Session of the EuroCarb ESF Network)

Convenors

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Sunday PO Session

MS10 : SUPO01 : PO

Some Geochemical Observations from the Carbonatites of the Proterozoic Tikshezero Massif (North Karelia, Russia)

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The Tikshezero massif is a part of the Kola-Karelian alkaline province. The greatest number of massifs of this region belongs to the Paleozoic time and are situated in Kola-Belomorian accretion-collision area. The Tikshezero massif is characterized by the age of 1.7-2.0 Ga (Belyatsky et al., 2000) and belongs to the N-W part of the Karelian craton. Carbonatites of the Tikshezero massif are represented mainly (90%) by a calcite type (sövite). In comparison with Paleozoic ones they are characterized by a comparatively low degree of differentiation, as revealed by the absence of clearly developed phosphorites. Magnetite and forsterite form scarce small aggregates. At the same time, apatite is uniformly distributed within the carbonatites and its average content is about 10%. Apatite composition reveals low differentiation in Ce and La contents (Ce₂O₃: 0.09-0.59, La₂O₃: 0.02-0.26).

Low degree of Tikshezero carbonatite differentiation is also demonstrated by the composition of rare metal accessory phases such as zircon, baddeleyite and pyrochlore. The zircons are characterized by rather low HfO₂ content in comparison with the zircons from Paleozoic carbonatites (0.18 vs. 1.52 wt.%) and higher REE content (1.20 vs. 0.17 wt.%). The same tendency is observed for baddeleyite. Pyrochlore of the Paleozoic complexes can be divided into the early and several later generations, but the pyrochlore of the Tikshezero carbonatites can be compared well with the early generation and is characterized by a higher Nb content (up to 71.87 wt.% Nb₂O₅). The baddeleyite crystals are zoned and contain inclusions of apatite, phlogopite, calcite and baddeleyite.

The Tikshezero carbonatites have a prominent enrichment in Cr and Ni, higher Ni/Co ratios and lower contents of PGE, Au, Ag in comparison with the Paleozoic carbonatite complexes. These features can be connected with less differentiation of the studied carbonatites. It could be suggested that low differentiation of the Tikshezero carbonatites correlate with the degree of differentiation of the primary magmas. It is proved by Cr content in picrite with respect to carbonatite of alkaline complexes - for the Tikshezero massif this ratio is 8.4 and for Kovdor massif, for example, 32. The comparatively high REE content, high Ba/Sr ratio and low Ti content in the Tikshezero carbonatites in the comparison with Paleozoic carbonatites correlate with such a tendency for a wider range of carbonatite complexes of the world both in age and space and reflect the specific evolution of mantle composition.

MS10 : SUPO02 : PO

Evidence for Plume-Lithosphere Interaction from Nd-Sr Systematics of Carbonatites and Kimberlite-Hosted Peridotite Xenoliths, Southwestern Greenland

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Results from melt experiments and Nd, Pb, and Sr isotopic data have clearly established that carbonatitic melts are of a deep-seated mantle origin. Numerous isotopic studies have already shown their effective use in monitoring the

chemical evolution of the subcontinental mantle (SCM). Moreover, their widespread occurrence in most continental settings over a significant interval of geologic history (e.g. from 2.7 to 0.1 Ga ago in North America; Bell & Blenkinsop, 1987; 1989) permits to monitor the temporal evolution of SCM. The age distribution of carbonatite occurrences world-wide are also well correlated to major orogenic cycles for the past 3.0 Ga (Woolley 1989). One interpretation is that carbonatite occurrences may result from the interaction between mantle perturbations or upwellings (i.e. "plume component") and continental lithosphere, such as in the East African Rift (Bell & Simonetti, 1996) or Deccan alkaline complexes of India (Simonetti et al., 1998).

The alkaline province of Greenland records repeated magmatic activity for >2.5 Ga (Larsen et al., 1983), and thus provides an opportunity to investigate the temporal variation of possible interaction between different mantle reservoirs. Moreover, recent experiments suggest a continuum exists in carbonatite-kimberlite melt compositions produced by variable amounts of melting at the source (Dalton & Presnall, 1998). One such example is that of the carbonatite-kimberlite-ultramafic lamprophyre association of the Sarfartoq region in west Greenland. Here we report on the Nd and Sr isotope systematics of the carbonatite complexes of Tupertalik, Safartoq, and Qaqarsuk ranging in age from 2700, 600, and 175 Ma, respectively. Initial ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr ratios for the whole suite vary from 0.51259 and 0.70343 (Qaqarsuk), 0.51201 and 0.70275 (Sarfartoq), to 0.50908 and 0.70126 (Tupertalik). This data plots along the established Sr and Nd isotopic temporal evolutionary trends defined by North American carbonatites (Bell & Blenkinsop, 1987; 1989), suggesting that the lithospheres beneath the North Atlantic and Superior cratons shared a similar history. In addition, an isotopic investigation was conducted of least contaminated peridotite xenoliths hosted by kimberlites temporally related to the 175 Ma (Attawapiskat region Superior craton) and 600 Ma (Sarfartoq, North Atlantic craton) events. These yield systematically lower initial Sr and higher initial Nd isotopic compositions compared to the associated carbonatites, indicative of derivation from a more depleted source. This feature also implies the involvement of a more "radiogenic" mantle component during carbonatite formation. Thus, the Sr and Nd evolutionary defined by the North American and Greenland carbonatites complexes may result from the mixing between a depleted SCM end-member with a more radiogenic component. Depleted subcontinental lithosphere may represent the former, whereas the latter component may be related to asthenospheric upwellings (mantle plumes) also giving rise to the kimberlite occurrences.

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MS10 : SUPO03 : PO

The Carbon Geochemistry of Terrestrial Impact Craters

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Terrestrial impact craters appear to be unique in the geological environment in that they contain evidence for all four allotropes of carbon: graphite, diamond, fullerenes and carbynes. Diamonds related to impacts were first observed at Meteor Crater, Arizona. In the early 1960s the observation of small diamonds associated with the Canyon Diablo meteorite led to speculation that they formed as a result of a high pressure and temperature associated with the impact. Opponents argued that needed heat and pressure could not have been achieved in such an impact, and that the diamonds were probably formed in space, during the formation of the meteorite itself. During the 1970's studies of the Popigai impact crater in Russia by Masaitis and others, revealed the presence of diamonds in the impact-produced rocks associated with the crater, clearly demonstrating that it was possible to form diamond in an impact. By the late 1990s impact-produced diamonds had been found associated with several other impact craters

including the 65 Ma old Chicxulub crater in Mexico, the 15 Ma old Ries crater in Germany, the 1.8 Ga old Sudbury impact structure and several others (see [1] for a review). Several mechanisms have been proposed for the formation of impact diamonds including the shock-induced martensitic transformation of graphite, quasi-liquid condensation associated with shock waves and vapor-phase condensation associated with impact plumes [1].

Important evidence on the temperatures associated with the transformation of carbon in impact events comes from the reported occurrence of another carbon allotrope, the controversial sp-bonded allotrope, carbyne (chaoite), first observed in the geological environment at the Ries crater by [2]. In laboratory experiments this allotrope is not stable at temperatures below 2000K, implying that carbon associated with the impact target rocks has experienced temperatures in this range.

The fullerenes C-60 and C-70 have been observed in shock-produced breccias from Onaping Formation of the Sudbury impact structure in Ontario, Canada by Becker et al.[3]. These authors suggested that the fullerenes were likely synthesized within the impact plume from the carbon contained in the bolide. The oxidation of the fullerenes during the 1.85 billion years of exposure was apparently prevented by the presence of sulfur in the form of sulfide-silicate complexes associated with the fullerenes.

Graphite is a common constituent of the target rocks in terrestrial impact craters as are various forms of sub-graphitic carbon and organic carbon. Recent studies of the Ries crater by [4] indicate that graphite also occurs in most of the impact-produced rocks, presumably acting as the source carbon for more exotic forms of carbon produced by the impact.

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MS10 : SUPO04 : PO

Phoscorites of the Vuoriyarvi, Turii Mys and Sebylavr Alkaline Complexes (Kola Peninsula, Russia): A Review

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Vuoriyarvi, Turii Mys and Sebylavr relating to the Kola Alkaline Province are typical highlybasaltic alkaline-ultramafic complexes with phoscorites and carbonatites stockworks. A noteworthy feature of these complexes is the variety of types and complex relationships of phoscorites with associated carbonatite and silicate rocks.

Phoscorites and carbonatites at Vuoriyarvi are developed as two distinct stockworks within the clinopyroxenites in the eastern part of the complex (Kogarko et al., 1995). One of them (Tukhtavara) represent the early phoscorite type composed of "classical" forsterite-magnetite and apatite-forsterite-magnetite rocks massive in structure, while the second one (Neskevara) consists essentially of coarse-grained submonomineralic magnetite and apatite-magnetite rocks usually extremely brecciated, recrystallized and cut by numerous veins of tetraferriphlogopite-calcite aggregate. The Neskevara phoscorites are considered to be later.

Phoscorites and carbonatites at the Turii Mys occur as a typical stockwork in the inner part of the Central massif (Kogarko et al., 1995). In contrast to the phoscorites described in Vuoriyarvi, the early ones from Turii Mys consist mostly of pyroxene analogues with much diopside instead of forsterite. The forsterite-bearing phoscorite is relatively rare in the Central Massif, which seems to be due to the low amount of olivine among the major silicate phases in the complex. Apatite-magnetite rocks are the dominant phoscorite type at the Turii Mys and represent the late phoscorite types. They are relatively coarse-grained, and the mineral proportions vary considerably.

The Sebylavr massif contains the numerous dykes and veins of phoscorites and carbonatites throughout the massif, but mostly to the north (Bulakh et al., 1998). Phoscorites at the Sebylavr massif represent a great diversity of types with apatite, diopside, phlogopite, tetraferriphlogopite, forsterite and magnetite as the major minerals.

Accessory minerals of the phoscorites in all the observed complexes include ilmenite, baddeleyite, calzirtite, zircone, zirconolite, zircon and pyrochlore. Structural-textural features point to magmatic crystallization of apatite, magnetite and forsterite (diopside) in the early phoscorites. Textures in the late phoscorite suggest a probable transition from pure magmatic to essential hydrothermal conditions. Mica appears to be primary in the late phoscorites. Normally calcite is a common mineral in all phoscorite types, but we believe that calcite as well as amphibole and serpentine are secondary minerals formed by intense metamorphic alteration of the igneous crystallization products by fluid components.

Bulakh AG, Le Bas MJ, Wall F & Zaitsev AN, *N.Jb.Mineral.*, 4, 171-192, (1998).
Kogarko LN, Kononova VA, Orlova MP & Woolley A, *Alkaline rocks and carbonates of the World. Chapman and Hall, London, UK.*, 2, (1995).

MS10 : SUpo05 : PO Experimentally Determined Trace Element Partitioning between Baddeleyite and Carbonatite Melts

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Baddeleyite (ZrO₂) is an accessory phase in a wide range of rocks ranging from kimberlites to carbonatites. Despite an increasing interest in baddeleyite especially in the fields of geochronology and petrology, there is, however, no experimental information as to how trace elements partition between baddeleyite and silicate or carbonate melts. To address this problem, hitherto unknown partition coefficients between baddeleyite and carbonatite melt were determined experimentally at high pressures and high temperatures. Experiments were performed at 1 GPa in a piston cylinder apparatus at Bristol. Experimental run products were analysed for trace elements with ion microprobe techniques. Calculated partition coefficients indicate that U, Th, Hf, Nb and Ta as well as the heavy rare earth elements (HREE) prefer to enter baddeleyite rather than carbonate melts (D>1), whereas the light rare earth elements (LREE) and other trace elements behave incompatibly (D<1), i.e. they prefer to enter the carbonate melt rather than the baddeleyite crystal. The experimental results are interpreted using lattice strain models and compared to bulk modulus data of Hazen and Finger (1979).

Hazen RM & Finger LW, *J. Geophys. Res.*, 84, 6723-6728, (1979).

MS10 : SUpo06 : PO Nomenclature of Phoscorites Exemplified by the Kovdor Massif, Kola Alkaline Province (Russia)

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The weighted average chemical composition of the multi-stage Kovdor Phoscorite-Carbonatite Complex (KPCC) recalculated to mineral norms gives (wt.%): forsterite=26.7, apatite=14.7, magnetite=32.3, and calcite=26.3. Consequently, variations in the modal composition of the KPCC rocks can be illustrated on diagram Forsterite-Apatite-Magnetite-Carbonate. To maintain consistency with nomenclature of igneous rocks approved by IUGS (LeMaitre, 1989), the boundary between carbonatites and phoscorites should be drawn at 50% of carbonate component. The major carbonate mineral in KPCC is calcite; dolomite rocks and ferrocyanatites are rare. Phoscoritic rocks are further classified using 90%, 50% and 10% relative abundances of the principal mafic minerals. For rocks containing >90% of forsterite, magnetite and apatite, we propose the root-names forsterite, magnetite and apatite, respectively. To reflect the presence of 10 to 50% of another principal mineral in phoscorite, an appropriate prefix is added to the root-name, e.g. apatite forsterite is a rock with >50% of forsterite, 10-50% of apatite, and both magnetite and calcite <10%. In the presence of two or three minerals whose content ranges from 10-50%, their names are also included in the prefix in order of increasing abundance, e.g. calcite-magnetite-apatite forsterite contains >50% of forsterite and >10% of each apatite, magnetite and calcite, in such a proportion that apatite>magnetite>calcite. For rocks containing 10 to 50% of each calcite, apatite, forsterite and magnetite, the generic

name 'phoscorite' should be used, compounded by addition of a prefix reflecting the relative abundances of principal constituents. If the abundance of one of the principal mineral is less than 10%, its name may be used as a modifier, as calcite-bearing apatite forsterite magnetite phoscorite. For abbreviations, it is convenient to use the initial letters for each of the principal minerals, i.e. AF for apatite forsterite, etc. The KPCC was formed in six stages; each of these produced a phoscorite-carbonatite pair. In each pair, the phoscorite and carbonatite components are similar in mineral composition, but differ in abundance of the principal minerals, and characteristic minor phases (<10%), including nepheline, cancrinite, micas, clinopyroxenes, amphiboles, garnet, ilmenite, titanite, zircon and pyrochlore-group minerals. The presence of these characteristic minerals may be reflected in a modifier, e.g. phlogopite-bearing apatite forsterite. The use of modal mineralogy, instead of major-oxide abundances, is also beneficial for petrologic modelling, as it relates synthetic systems to their naturally occurring equivalents. Investigation of the evolutionary paths of magmas in the system Forsterite-Apatite-Magnetite-Calcite will be able to shed light on many problems concerning the genesis of carbonatite complexes. Supported by INTAS grant 97-0722 and RFBR grant 00-05-64174.

MS10 : SUpo07 : PO Hydrocarbons in Nepheline-Syenite Complexes of the Kola Alkaline Province (Russia): Direct Samples or Crustal Derivative of Mantle Carbon?

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Unusually high, for magmatic suits, concentrations of hydrocarbon compounds, gaseous especially and liquid and solid as well, in the rocks of the Paleozoic (~370 Ma) world's largest Khibiny and Lovozero nepheline-syenite plutons are known for almost half of century. Nevertheless, their origin and possible carbon sources are hitherto debated. Abiogenic intrinsic nature of hydrocarbons of these massifs has rather reliably revealed through carbon isotope composition and essential absence of organic carbon in Precambrian host sequences. Some researchers via thermodynamic calculations and experimental study of mantle-derived rocks base possibilities of formation and stable existence of varied hydrocarbon compounds in the mantle conditions. Prolonged, up to now, transmagmatic flow of hydrocarbon gases from crust depths and even mantle is allowed for the Khibiny and Lovozero. Our recent study of noble gas isotope compositions in the rocks of the Kola alkaline-ultrabasic with carbonatites and considered nepheline-syenite complexes evidences the common fluid sources to them with a predominance of the upper mantle and pronounced lower mantle contributions. C³He ratios (where C is carbon of hydrocarbon gases, mainly methane) comprising around 10⁹ and corresponding to these in the mantle are gained by means of bulk elemental and isotopic analyses of fluid inclusions in the Khibiny and Lovozero rocks. However, the results of fluid inclusion thermometry and thermodynamic modeling, hydrogen isotope compositions of hydrocarbon gases and associated H₂, distribution pattern of hydrocarbons in minerals, trends of correlations between ratios of individual gas components and features of mineral chemical compositions suggest that in cases of nepheline-syenite complexes, carbon was taken from the mantle as dioxide being dissolved in silicate melts and production of hydrocarbons occurred through vapour-mineral interactions according to the known Fisher-Tropsch reaction between carbon dioxide and hydrogen, predominantly during postmagmatic stages of rock formation. This study was supported by Russian Foundation for Basic Research, grant 00-05-64174.

MS10 : SUpo08 : PO Ultramafic Xenoliths and Xenocrysts at Mt. Vulture (Basilicata, Southern Italy): Petrological Evidence for Mantle Metasomatism and its Significance

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Mt. Vulture Quaternary melilite-carbonatite lapilli tuffs contain abundant thezolite, wehrlite, minor phlogopite-clinopyroxene and amphibole-peridotite xenoliths, along with pargasitic amphibole xenocrysts. Group A ultramafic xenoliths are anhydrous while group B are hydrous and contains amphibole and clinopyroxene xenocrysts. Incomplete transformation of orthopyroxene in clinopyroxene, Mg-rich interstitial phlogopite in peridotitic xenoliths and high pressure amphibole are suggestive of modal mantle metasomatism. Clinopyroxene incompatible trace element composition from group A porphyroblasts, group B xenocrysts and porphyroblasts after orthopyroxene are enriched with respect to primitive mantle, suggesting cryptic mantle metasomatism. Clinopyroxenes also show consistent trace element patterns and are depleted in HFSE, but enriched in LILE and LREE. Pargasitic amphibole in amphibole-peridotite and amphibole xenocrysts show consistent incompatible trace element concentrations and patterns that are similar to clinopyroxene. Amphibole REE patterns describe a linear enrichment from HREE to Nd while the LREE show a convex upward trend similar to that of the amphibole in veined peridotite xenoliths occurring at Ahaggar (southern Algeria). Petrography and mineralogy of the samples studied suggest that the mantle beneath Vulture has been modified by a metasomatic event responsible for the transformation of Iherzolite (and harzburgite?) wall rocks into wehrlite, crystallisation of interstitial phlogopite and pegmatoid amphibole in mantle veins. Cryptic metasomatism possibly accompanied modal metasomatism. This is reinforced by the similarity of LREE enrichment in HREE and MREE of amphiboles and clinopyroxene of both groups, which expressed as La/Er and La/Dy describes a linear trend. Glass trapped in the reaction corona around orthopyroxene may represent the residual of the metasomatic agent, which would have been a carbonated, Ca-rich undersaturated silicate melt. A subsequent, limited carbonatite metasomatic phase is recorded in the amphibole which has been partially transformed in fassaitic clinopyroxene.

MS10 : SUpo09 : PO Carbonatites in the Ayopaya Alkaline Province, Eastern Cordillera, Bolivia

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Carbonatites and carbonate-rich igneous rocks occur in the Ayopaya alkaline province in the eastern Cordillera of Bolivia as numerous, m-sized lenticular outcrops and as the 0.5 x 2 km large Chiaracke intrusion. The Chiaracke complex is the unique carbonatite complex in the Andes. The carbonatites are associated with sodalite-rich nepheline-syenitic to foyaite stocks, melilite-nephelinitic breccia diatremes and alkaline dikes of nephelinitic to basanitic-, phonolitic and alkali-lamprophyric composition. The carbonatites consist of Ca-Mg-Fe carbonates, together with apatite, fluorite, clinopyroxene, biotite, amphibole, feldspar, pyrochlore, baryte, bastnaesite, pyrite and magnetite. Small carbonatite lenses display transitional contacts into carbonate-rich siliceous rocks with aillikitic affinity. Geochemically, the carbonatites have predominantly magnesio- to ferrocyanatitic, rarely calcicarbonatitic composition. The carbonatites are strongly enriched in LREEs, with up to 3000 ppm La and 4500 ppm Ce, and

total REE contents up to >1.3 wt%. Also enriched are other incompatible elements such as Nb, Sr, Ba and Th. Isotopic data indicate a common mantle origin for the entire magmatic rock suite of the Ayopaya alkaline province (ϵ_{Nd} -1.2 to +4.1). The alkaline magmatism of the Ayopaya region is related to Cretaceous rifting during the opening of the Atlantic Ocean. K-Ar data on phlogopite megacrysts define an age of 100 Ma (100.7 ± 1.2 , 99.0 ± 1.1 Ma). Recently found alluvial diamonds from the Rio Ayopaya are probably related to the alkaline rock suite although a specific magmatic host rock could not yet be defined.

MS10 : Supo10 : PO New Mechanism of Diamond Crystallization

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The majority of the investigators holds the opinion that the diamonds can be formed by ultra high pressure and temperatures. However modern experimental conditions of a diamond synthesis and theoretical data allow to make essential additions to the theory of diamond formation and prospecting of new origin deposits of diamonds. For the example the results of the experimental work spent by us can to demonstrate a new mechanism of diamond crystallization. Experiments have been carried out to synthesize diamond film on skeleton metamorphic diamond seeds. The goal of the work was to study the possibility to fill in negative forms and bind minor skeleton diamonds together to form a single polycrystalline aggregate. The synthesis was performed under the atmospheric pressure and the temperature not exceeding 450°C on the surface of grains from the skeleton metamorphic diamond powder through nonstable b-carbine. Carbine - diamond transformation proceeded in a solid-phase medium, although some participation of a gas phase, formed by sublimation of nonstable portions of the film, was not ruled out. As suggested by X-ray structural analysis, the resultant film comprises several phases and has the following X-ray data (nm): 0.330 (2); 0.288 (10); 0.231 (5); 0.2045 (10); 0.1933 (1); 0.1479 (1); 0.1296 (4); 0.1090 (1); 0.0935 (1); 0.0904 (1); 0.0881 (1). Observed in the film were carbon phases other than the diamond one: graphite, chaoite, b-carbyne. Electron microscopy revealed the polycrystalline nature of the synthesized film and the character of the growing phase precipitation on the surface of the diamond seed. As the experiment progressed, separate seed grains lost their mobility relative to each other and came to be bound by the growing film. The result suggests that diamond crystallization is possible at the atmospheric pressure and this method can be perspective to improve technical characteristics of natural diamond single crystals. An important feature of the process is its low energy demand. This data are very important for creation of a modern diagram of carbon state and prospecting of new types of diamond deposits.

MS10 : Supo11 : PO Ba-Sr-REE Mineralisation in the Sallanlatvi Carbonatites, Kola Peninsula, Russia as a key to Understanding the Evolution of Late Stage Carbonatites

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The Sallanlatvi carbonatite complex is unique in the Kola Alkaline Province in that it contains much magnesite and siderite-bearing carbonatite. It contains varieties of carbonatite dominated by each of the main rock-forming carbonate minerals: calcite, dolomite, ankerite, magnesite-dolomite and siderite. The REE-, Sr-, Ba-bearing minerals: ancyllite, strontianite, and barite are typical accessories in all carbonatite types at Sallanlatvi and are being used to track the evolution of the carbonatite complex. The first stage is to define the paragenetic sequence and variation in mineral compositions. The modal proportion of REE-, Sr-, and Ba-bearing minerals increase from earliest (calcite) to

latest (siderite) varieties of carbonatite. There is textural evidence that the association ancyllite, strontianite, and barite crystallised late in all of the Sallanlatvi carbonatites but there is considerable variation in composition throughout the carbonatite sequence. Ancyllite-(Ce) occur in a number of carbonatite complexes world-wide but has been studied very little. It is the most common REE-rich mineral at Sallanlatvi, occurring as euhedral rhombo-dipyramidal or prismatic crystals, usually in irregular patches and veinlets. The degree of light REE-enrichment in Sallanlatvi ancyllite is most extreme in the early calcite carbonatite, resulting in the rare composition ancyllite-(La). High contents of Fe and Th, lower contents of total REE and lower La/Ce ratio occur in ancyllite from later carbonatites. The temporal sequence of carbonatites cannot be explained as a straightforward sequence of fractional crystallisation. Monazite was found associated with ankerite in dolomite and magnesite-dolomite carbonatites, where it fills cracks in dolomite. It occurs as prismatic crystals or botryoidal aggregates/Strontianite is present in platy crystals or botryoidal aggregates, growing on walls of cavities. The contents of Ba and Sr in the mineral are highly variable in different carbonatite types. The highest concentration of barite occurs in the latest siderite carbonatites at Sallanlatvi, where it forms vein-like aggregates. In other Sallanlatvi carbonatites barite forms well-shaped dipyramidal crystals growing on ancyllite and strontianite. There are few chemical impurities in the barite and so very little variation in composition through the carbonatite sequence. The rare barium zeolites-harmotome and edingtonite founded in calcite carbonatites in association with described minerals complete given series of minerals. A similar pattern is observed in the evolution of the chemical composition of pyrochlore group minerals at Sallanlatvi. The earliest varieties to crystallise were pyrochlore sensu stricto and uranoan pyrochlore, while bariann- and strontio-pyrochlore appear at the end of carbonatite-formation. This study was supported by INTAS - 97-0722 and RFFI-98-05-64365.

MS10 : Supo12 : PO New Extrusive Carbonatite Occurrence in Central Italy: The Volcanic Field of Oricola-Camerata Nuova, Abruzzo, Central Italy

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The volcanic field is comprised of several Upper Pleistocene tuff rings and maars, aligned along a NNW-SSE normal fault of regional meaning. Characteristic sequences of ash lapilli tuff surges and vent coring etrolithic breccias are well exposed. Most of the deposits are directly related to vent structures. In addition, the presence of welded lapilli and ballistic impacts accounts for a proximal local origin of the hosting tuffs. Geological context, age, mineralogy and petrology are germane to the near Grotta del Cervo occurrence (Comodi et al., 1999) and ULUD (Lavecchia and Stoppa, 1992), which consist of carbonatitic-kamafugitic rocks (Stoppa and Wolley, 1996).

At Oricola-Camerata Nuova volcanic field, juvenile fragments and tuffs range from phonolitic-foitide to foititic-carbonatitic to carbonatite s.s. The latter forms small pyroclastic flows and relatively large surge deposits which, in recent times, have a unique parallel in the Fort Portal volcanic field, Western Uganda. Juvenile fragments consist in plastically moulded lapilli, essentially composed of diopside, phlogopite, leucite, K-feldspar, apatite and immersed in a turbid micro-crypto crystalline matrix of Ca-carbonate. Lapilli shape indicates that they agglutinated and quenched when still hot plastic. Silicate glass shards are present and have typical cusped wedges produced by bubbles expansion and disruption during strombolian activity sustained by juvenile gases. Silicate and carbonate microspherules (Peele tears-like) testify for low viscosity melt. This is consistent with high temperature, juvenile gas (CO₂)-triggered eruption of coexisting phonolitic-foitide and Ca-carbonatite.

Multielemental, mantle-normalised pattern conforms and is in the range of ULUD carbonatites and kamafugites but with slightly higher Ba, Rb and Th. Sr isotopes indicate substantial equilibrium between carbonate and silicate

phases and in a range which is well clear from possible sedimentary carbonate value. These data, coupled with high Sr, Ba contents of calcite and Mg-calcite, testify for a magmatic primary origin of the ground mass carbonate. Presence of K-feldspar and phonolitic terms in ULUD suite has been proved being a consequence of liquid evolution after carbonatite immiscibility and CO₂ exsolution (Stoppa and Cundari, 1998).

This new carbonatitic outcrop, that joins the increasing number of Italian carbonatites, puts Italy in a relevant place for what concerns carbon-rich mantle magmatism occurrences. Actually, the six extrusive carbonatites and the intrusive one so far reported, represent one of the largest concentrations of such a kind of rocks all over the world.

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MS10 : Supo13 : PO Extrusive Carbonatite-Melilitite and Tuffite at Ruri Volcano (West Kenya): The High Explosive Counterpart of Carbonatite-Mafic Alkaline Ring Complex

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Subvolcanic carbonatite ring complexes may have an eruptive counterpart in high energy carbonatitic-melilititic eruptions. The Ruri volcano, part of the nephelinite-carbonatite district of Homa Bay in West Kenya, is typically bimodal with a subvolcanic association of ijolite-sövite-syenite coupled with carbonatitic and melilititic pyroclastic rocks. Four kinds of breccias and tuffs have been recognized at Ruri, based on rock structure and texture, the nature of fragmental materials and matrix relationships. They are: 1. Etherolithic breccia, a mixture of accidental fragments with no obvious juvenile component. 2. Pelletoidal etherolithic breccia, which is a typical tuffite with rounded, mafic high pressure xenocrysts, having a thin coating of melilititic glass, in a carbonatite matrix. 3. Lapilli-tuff of cored lapilli with a concentric arrangement of melilitite laths around a solid kernel of clinopyroxene or spinel in a carbonate matrix. 4. Lapilli ash tuff to scoria agglomerate. Depositional mechanisms vary from subvolcanic emplacement of conduit fluidized lithic and juvenile material to eruptions producing mostly dry surges or proximal ballistic deposits. High temperature flattening and welding of carbonatite juvenile lapilli have been detected in 3 above. The juvenile component increases progressively from 1 to 4, possibly indicating shallower levels of magma fragmentation in the conduit or lesser involvement of the sub-stratum. This means, in volcanological terms, a change from volcanian to strombolian activity. No effects of magma cooled by water or phreatomagmatic features have been detected at Ruri, and it is presumed that the highly explosive character was produced by exsolution of CO₂. The Ruri rocks contain ultramafic debris, notably Cr-rich, Al-poor diopside, unstable and strained phlogopite and olivine, which indicate possible desegregation of mantle rocks. At Ruri melilititic liquids are co-eruptive with igneous carbonate. The melilitite has no intrusive equivalent in the Ruri volcano and may represent a primitive parental magma. Unfortunately, this cannot be represented by a conventional bulk rock composition, owing to the mixed nature of the volcanics. At melilititic liquidus temperatures and at low pressure, carbonatite is a very low viscosity and immiscible liquid. It may have been erupted mainly as fine sprays of droplets and ash fragments, which now form the tuff matrix. High and lower temperature extrusive calcite and primary intrusive calcite can be distinguished from recrystallised calcite by chemical composition and texture.

MS10

The Role of Mantle Carbon in the Global Carbon Cycle

MS10 : SU014 : PO

A New Kamafugite Occurrence from Abruzzi, Italy-The Kalsilite Melafoidite from Grotta Del Cervo

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A new kamafugite occurrence near Pietrasecca, in the eastern Apennine Abruzzi region of Italy, is described in detail to characterise its paragenesis and to establish possible genetic links with similar assemblages from the coeval Umbria-Latium-Ultrapotassic-District (ULUD). This is formed by rare kamafugites and carbonatites associated in time and space with the much more voluminous Roman Region Lavas, RRL, of Recent age, forming a belt of about 6000 sq. km along the western coast of Central Italy. The new kamafugite was found in a cave known as Grotta del Cervo, GC, associated with epiclastic eruptive rocks. Lapilli ash tuff, welded lapilli, ultramafic xenoliths, cognate lithics and pelletal lapilli have been identified. The mineralogy of the welded lapilli (GC-1) is represented by diopside leucite, haitiynite, estonite, andraditic garnet, apatite, magnetite, kalsilite, olivine, and carbonate, listed in order of decreasing abundance. Variable proportions of the same mineralogy was found in the associated rocks. The bulk-rock chemistry of GC-1 classifies as a kamafugite according to Sahama (1974), closely approaching the composition of ULUD San Venanzo kamafugite (olivine melilitite). The lapilli ash tuff (GC-2), characterised by the same silicate mineralogy as that of GC-1 plus modal carbonate exceeding 10%wt is a carbonatitic kamafugite, similar to the San Venanzo analogue described by Stoppa (1996). Bulk-rock and trace-element compositions confirm that the GC rocks closely approach the San Venanzo analogues. Absence of melilitite and rare olivine and the possible role of phlogopite in the GC assemblages was discussed in detail by Cundari and Ferguson (1991). Na availability to melilitite crystallization was reduced by haitiynite crystallization, reflecting an increasing and progressive increment of Na in ULUD assemblages, relative to K, regionally from North to South and culminating with the occurrence of abundant haitiynite in the Vulture assemblages. Notably, this general trend is also observed in the RRL rocks, although it is less pronounced in the latter province. The GC occurrence partially fills the gap between ULUD rocks and the Vulture Complex, both in terms of geography and mineralogy, and adds considerably to the number of the very rare rocks of kamafugitic affinity, which may further extend southward towards Vulture.

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MS10 : SU015 : PO

Economic Deposits Associated with Carbonatites: Their Formation and Use in Understanding Mantle Carbon

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When carbon travels from the mantle to the crust to form carbonatites, it brings with it a variety of elements of economic interest. Carbonatite complexes are mined for niobium, rare earth elements, copper, iron, baddelyite, phosphate, vermiculite and fluorite. The study of the processes required to form carbonatite-related ore deposits not only helps to improve the exploration and exploitation of these resources but can also contribute to a more fundamental understanding of the production and emplacement of rocks containing mantle carbon. This is one of the topics for the second ESF Eurocarb Network workshop in Finland, September 2001.

Ore-forming processes in carbonatites can be divided into three stages or types: (1) concentration of the elements of interest in the original carbonate-bearing melt in the mantle (2) enrichment via petrogenetic processes, such as fractional crystallization and evolution of fluids in the crust, and (3) reworking of carbonatitic rocks by later hydrothermal fluids and weathering. Most deposits require a concentration mechanism in addition to (1) and carbonatite diatremes containing mantle material are rarely of economic interest, except possibly for diamonds.

Most niobium deposits are produced by weathering which concentrates the Nb ore mineral, pyrochlore. It is noticeable, however, that in most cases, the precursor fresh rocks also contain above average concentrations of pyrochlore and are rich in silicate minerals. The apatite-magnetite-mica rocks at Sokli, Finland are an example of this. The formation of these ores requires concentration of Nb in a carbonate-bearing melt in the mantle and then, probably, a cumulate process to separate the apatite-magnetite-mica from the main carbonatite.

REE deposits in carbonatites can also be produced by weathering and hydrothermal reworking. Some however, are produced from REE-rich magmas and their exceptionally high Nd and Sr concentrations are potentially very good for providing information on mantle source characteristics. Most of these REE-rich carbonatites have "normal carbonatitic" isotopic signatures. Their light REE-enrichments are consistent with production by small degree partial melts of a depleted mantle source and then a further stage of enrichment in the crust. However, the World's two largest carbonatite, or carbonatite-related, REE deposits at Mountain Pass, USA and Bayan Obo, China are unusual because they have Nd and Sr isotopic signatures indicative of enriched mantle sources.

There is also information to be gained from looking at the distribution of REE-rich carbonatites. Some regions, such as the South African craton, have many carbonatite complexes but no REE-rich carbonatites. The REE-rich carbonatites are concentrated to the north and associated with the East African rift valley structure.

Monday PM Session

MS10 : MOPm21 : G8

Mantle Carbon and Global Carbon Fluxes; A Planetary Review

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Estimated bulk Earth's carbon (5.97×10^{24} kg) is inequally distributed between two reservoirs where (i) superficial carbon (sediments, climate and aqueous C) = 5.4×10^{19} kg is dwarfed by (ii) solid carbon (crust, mantle, core) = 5.9×10^{24} kg (ref1). Current day annual C fluxes between individual C sinks of (i) are known in considerable detail, with measurements for example of organic and inorganic C from photosynthesis, ocean-climate exchange, biomass, sediment, soil and snow fluxes. Superficial carbon fluxes, and carbon in the carbon cycle constitutes about $100-400 \times 10^{10}$ kg. Fluxes estimated in the early 1990's for volcanic carbon (0.1×10^{10} kg CO₂) are generally small in comparison to fossil fuel combustion, which is intensively studied due to its likely effect on climate warming (5×10^{10} kg). If the carbon flux data is taken at face value, then every molecule of superficial carbon (i) on Earth could be recycled (organic and inorganic) in approximately 10⁷ years, or 10 my; but the solid carbon (ii) would not be recycled even in 10¹⁶yr, or 10,000 Gyr. It is interesting that over the lifespan of the Earth (4.6 Gyr), all the superficial carbon (i) could have been derived by degassing of solid carbon (ii) through volcanic degassing. However, since the solid carbon reservoirs (ii) are so enormous, the variation of even a small flux becomes highly significant over geological time, and it becomes imperative both to establish how primordial carbon is degassed, and to quantify any feedback systems, such as subduction. More recent data revises the fossil fuel flux upwards by up to 2 orders of magnitude (5×10 kg C) but comparable quality flux revisions for volcanic C are lacking. Modelling over various timescales is widely seen as reliable, but the results are only as good as the data input. What can be done by the volcanic community (senso lato)? We need to know much more about the volcanic flux of C from the mantle, and whether or not release over longer time scales is continual, episodic or catastrophic. For comparison the single Chicxulub impact perhaps released ~10e16 kg CO₂, or more than 1 million times the global annual volcanic flux in a few hours (ref2). The steady state volcanic C flux over the short term can be broken down according to tectonic setting, such as subduction, mid ocean ridges, etc. Constraining estimates for the carbon sinks and flux from (ii) represented primarily by volcanic carbon, including the perspective of geological hindsight, must surely be a major objective for the future.

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MS10 : MOPm22 : G8

Carbon Flux Through Time

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Carbon geochemistry is commonly presented in terms of cycles, ranging in scale from biogenic to orogenic. Description of element behaviour patterns in cyclic terms is attractive, convenient, and risky. Danger lurks in a temptation to see the cycle as a closed loop, and in the case of carbon this often proves irresistible. Faced with a process that could involve juvenile carbon, some Earth scientists prefer to invoke re-cycled sediment. For particular cases this may be justified, but to elevate these to the status of a general explanation is to lock into an intellectual closed loop. Carbon contents in sedimentary reservoirs are several orders of magnitude greater than those involved in the present surface cycles, which are but an appendage to a pattern of continual carbon release from the deep Earth through geologic time. A similar pattern is revealed in volcanic gas emission rates, which are commensurate with progressive filling of the surface/crust reservoirs over the Earth's history. Subduction of sediment only adds further to the budget excess, because present thinking favours the view that any carbon may persist for long periods, and is thus effectively sequestered in the mantle. A small

proportion of diamonds may be ascribed to re-cycled carbon, but most have C isotope compositions with no sign of crustal or organic antecedents, and may represent pristine samples of the mantle carbon that has been supplied to the sedimentary reservoirs through time.

Rates of carbon release from the deep Earth have fluctuated through time, the best documented case being the Cretaceous Magnetic Quiet Zone (CN superchron). Enhanced levels of carbonite and kimberlite activity are matched by global increases in volcanicity and sedimentation, changes in sea floor spreading rates, sea levels, chemical stratigraphy, and in plate motion patterns and velocities. Such correlations may be linked with the geophysical inference that the CN superchron marks a critical perturbation in core dynamics over this period.

There are many imponderables in the release patterns of carbon from the Earth, leaving much scope for discussion and new research initiatives, but the continual release of juvenile carbon during geologic time means that re-cycling sedimentary carbon, through orogenic or subduction zones, has never been more than a sub-plot of the main story. Unless the total flux is kept in view, there are the risks of losing sight of: i. juvenile inputs to the exogenic system (and their possible impacts); ii. the range of mechanisms by which the system handles excess CO₂; and iii. constraints that may apply in the evolutionary history of the planet.

MS10 : MOpm23 : G8 The Formation of Mantle Diamonds

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Diamonds provide a rare opportunity to study pristine samples of mantle carbon. Still, it must be born in mind that most diamonds that reach the surface originate at a few limited regions of the upper mantle. Pressures and temperatures of diamond growth determined from inclusion chemistry, nitrogen aggregation and internal stresses in and around inclusions indicate that the majority of the diamonds that reach the surface of the earth were formed at pressures of 4.5-7.5 GPa and temperatures of 950-1350°C. Laterally, most diamonds are brought by kimberlites and related magmas that sample the mantle below old continental regions. In these regions, diamonds grew in two suites of rocks, peridotites and eclogites, as indicated by the mineralogy of their inclusions and the composition of diamondiferous xenoliths in kimberlites. Rare diamonds carry inclusions with minerals that are stable at pressures and temperatures prevailing at the transition zone or even deeper, at the lower mantle. These deeper diamonds as well as new occurrences of diamond outside the old cratons indicate that diamond may grow in other mantle environments as well.

The sources of the carbon for diamond formation in the mantle are debated. The wide range of carbon isotopic compositions of eclogitic diamonds is attributed to either isotopic fractionation of mantle carbon or to introduction of crustal carbon into the mantle via subduction. Transport of carbon into the eclogitic and peridotitic host rocks may be done in the form reduced species (e.g. methane) as suggested by inclusions of iron+wustite+olivine in some diamonds. However, observations of carbonates and carbon dioxide in fibrous diamonds suggest transport of carbon in its oxidized forms. The recent findings of oxidized fluids in UHP metamorphic diamonds and, together with either peridotitic or eclogitic inclusions, in octahedral kimberlitic diamonds suggest that oxidized species are common and play an important role in diamond formation. Experiments at high pressure and temperature also indicate the ease of diamond growth from oxidized fluids and melts.

MS10 : MOpm24 : G8 Carbonatite Magmatism: Constraints on the History of Carbonate Sediment Recycling in the Upper Mantle Since the Archaean

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The existence of isotopically distinct mantle components or reservoirs (HIMU, EMI, EMII, DMM, PREMA/FOZO) is now widely accepted, defined primarily on the basis of the Sr-Nd-Pb isotope composition of young oceanic basalts (MORB and OIB). How such reservoirs evolved isotopically, where they reside in the mantle, and when and how they first originated remain, however, subjects for speculation. As there are few samples of MORB and OIB older than 200 Myr, we need to find an appropriate proxy to constrain the isotopic evolution of the mantle.

Carbonatites occur on every continent on Earth, ranging in age from Archaean to recent. These unusual, low-degree, partial melts of carbonated peridotite appear to be derived from the same mantle source as OIB (Oceanic Island Basalts) over the past 200 Myr. As their primary Sr-Nd isotopic signatures are largely buffered against crustal contamination, (because of high Sr and REE concentrations), these data can be used to track the geochemical evolution of the mantle reservoirs which they sample. Identifying the time at which magmas derived from isotopically distinct mantle reservoirs first reached the Earth's surface provides important constraints on the role of sediment subduction and mantle convection in the generation of mantle heterogeneity.

Most Precambrian carbonatites appear to be derived from a trace element-enriched mantle source with age-corrected Sr-Nd isotope characteristics similar to PREMA (Stein & Hofmann, 1994) or FOZO (Hart et al., 1992), which we consider is a lower mantle reservoir sampled by upwelling plumes. Depleted mantle (DM) does not appear to be involved in their petrogenesis. During the Phanerozoic, however, the number of mantle reservoirs contributing to carbonatite magmatism appears to increase. In the last 200 Myr both HIMU and EM source components become increasingly dominant. The wide range of Sr-Nd-Pb-C-O isotope signatures of Phanerozoic carbonatites in contrast with the PREMA-like signatures of those of pre-Phanerozoic age, suggests that the eruption of HIMU-EMI-EMII magmas on the surface of the Earth may be a Phanerozoic phenomenon. This observation has profound implications for models of mantle geodynamics.

Using published Nd-Sr-C-O isotope data, we demonstrate the increasing importance of a recycled pelagic carbonate sediment component in the mantle source of Phanerozoic carbonatites. There is no evidence for significant biogenic carbon recycling in the C isotope signatures of any of the carbonatites in our data set. Whilst recycled pelagic carbonate may provide a significant C reservoir for carbonatite genesis, we note that carbonate sediments have low REE contents, quite unlike carbonatites. Thus, while the $\delta^{13}\text{C}$ isotopic signature of a carbonatite may reflect a significant pelagic sediment contribution, its Nd isotope signature will most likely be decoupled, reflecting that of the ambient mantle at the time of melting.

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MS10 : MOpm25 : G8 Fibrous Diamonds in an Eclogite Xenolith from the Mbuji Mayi Kimberlites (Congo)

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A large collection (160 samples) of eclogite xenoliths from the Late Cretaceous Mbuji Mayi kimberlites (Kasai, Congo) were investigated by El Fadili and Demaiffe (1999). One nodule was diamondiferous. After careful hand-picking, sixteen microdiamonds (from 1.0 to 0.1 mg, mean = 0.5 mg) were recovered, two being clearly identified as inclusions in garnet. Observation reveals that none of the diamonds are of gem quality. In contrast, all were opaque-like (hence no FTIR data available), 12 being clearly cubic, resembling the fibrous diamonds (which predominate in the diamond production from Mbuji Mayi kimberlites) frequently overlying an early formed, octahedrally-shaped, gem quality core.

The bulk analyses (C and N isotopic compositions and N concentrations) on 14 samples confirm these suggestions: the $\delta^{13}\text{C}$ -values range from -7.41 to -6.42 ‰ (mean = 7.15), $\delta^{15}\text{N}$ -values from -4.3 to -2.5 ‰ (mean = -3.3) and N-contents from 1225 to 1994 ppm (mean = 1500). These values are within the worldwide range of fibrous diamonds reported previously (i.e. $\delta^{13}\text{C}$ from -8 to -5 ‰, $\delta^{15}\text{N}$ from -8 to -2 ‰ and N-content from about 800 to 3350 ppm (Javoy et al., 1984; Boyd et al., 1994; Cartigny et al., unpub. data)) and very different from peridotitic and eclogitic diamonds (which in both cases display more variable $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and much lower N-contents). In detail, however, the mean $\delta^{13}\text{C}$ -value for the fibrous diamonds of the eclogite falls on the lowermost side of Mbuji Mayi fibrous diamonds, whereas mean $\delta^{15}\text{N}$ and N-content values fall on the uppermost side. Within the rather restricted range of variations, no correlation was found between the different parameters.

These results clearly favor diamond formation within this eclogite from carbon-rich fluids related to the kimberlite magma; that means that the carbon has been brought within the eclogite after its formation. The fact that bulk analyses show isotopic features very similar to other fibrous diamonds demonstrates that the core of the diamond is small enough to be neglected. In other words, most of the carbon, if not all, now present within the eclogite xenolith is not related to the eclogite formation, whatever the eclogite is mantle-derived or of subducted origin.

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MS10 : MOpm26 : G8 Linking HIMU Subducted Slabs with Oceanic Carbonatites: The High Nb/Ta Cape Verde Carbonatites

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The carbonate component of subducted oceanic slabs react itself away in the convecting upper mantle and ceases to be a concentration. Not so where the lithosphere remain stationary in relation to the inferred plume, as on Cape Verde. Isotopic compositions of Sr, Nd and Pb, and concentrations of Nb and Ta of carbonatites from five islands in Cape Verde are reported. The carbonatites have relatively small variation in $^{143}\text{Nd}/^{144}\text{Nd}$ but large variation in radiogenic Pb. Compared to co-existing basaltic rocks, the carbonatites form a distinct Pb isotopic trend that extends to very high $^{206}\text{Pb}/^{204}\text{Pb}$, and to very high Nb/Ta ratios. Significant Pb isotopic differences between basaltic rocks and carbonatites from individual islands as well as between basaltic rocks and carbonatites as groups, are evidence of their origin from separate sources. The presence of carbonatites on HIMU islands, the very radiogenic lead of the carbonatites, and the high Nb/Ta ratios, indicate a recycled origin for the carbonate component. Carbonatite polluted

source regions of extreme HIMU localities Rurutu and Tubuai, exemplify the generic link between recirculation of carbon and oceanic carbonatites. The high Nb/Ta ratios of the carbonatites may represent the hitherto unknown high Nb/Ta reservoir associated with eclogite subduction

MS10 : MOPm29 : G8

Isotopic Regional Zoning Versus Tectonic Polarity in Pleistocene Leucitites, Melilitites and Carbonatites of the Italian Peninsula

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Pleistocene volcanism in the Italian peninsula occurs in two parallel but separated belts extending about 400 km along the Apennines. The first is the type-area for leucitites, (Washington's famous Roman Region), consisting of gigantic-caldera sheet-volcanoes and minor strato-volcanoes, which rest on stretched crust along the Tyrrhenian coast. Lithosphere thickness in this area is about 60 km. The second is the Intramountain Ultralkaline Province (IUP of Lavecchia and Stoppa, 1992) characterized by monogenetic carbonatitic-melilititic centres, but includes the long-lived Vulture volcanic complex. The IUP has experienced intense extensional crustal seismicity and has a lithosphere that averages 90 km. Although the two provinces are not considered co-magmatic, given the different tectonic styles and lithosphere thickness, they clearly relate to a similar source composition and geodynamic environment. The Italian association of carbonatites, leucitites, and melilitites is only mirrored by the western branch of the East African Rift Valley System. An interesting feature that emerges from a compilation of isotopic ratios is that ⁸⁷Sr/⁸⁶Sr (0.7112 - 0.7055), ¹⁴³Nd/¹⁴⁴Nd (0.5119 - 0.5127) and ²⁰⁶Pb/²⁰⁸Pb (19.37 - 18.74) isotope ratios systematically vary from north to south in both provinces. Nd-model ages are about 1.9 Ga in the north and decrease regularly until they reach 500 Ma in the south. In conventional Sr, Nd and Pb isotope diagrams RR and IUP rocks plot in the "enriched" quadrant along a line linking Group II kimberlites and Australian lamproites trending towards an enriched mantle end-member. Notably, kamafugitic-carbonatitic rocks from the northern section of the IUP province may reflect interaction between an EMII component and depleted mantle. This may reflect a single recent mixing event between two mantle end members, one enriched and the other depleted in terms of their isotopic signatures. This is consistent with the near primary nature of the IUP melts as evidenced by very high Mg# in bulk rocks and minerals, extreme SiO₂ under-saturation, very high Ni+Cr contents and an abundance of mantle debris. Isotope ratios in primary carbonatites-melilitites are insensitive to crustal assimilation having Sr and Nd abundances one to two orders of magnitude higher than sedimentary limestones. So far, the models proposed for Italian volcanism has been interpreted either in terms of subduction or continental rifting. The isotopic north-south polarity that we have found places important constraints on any tectonic model and we attempt to assess these models in terms of subduction, continental rifting, and plume activity. In the case of subduction or rifting, the polarity of tectonics is W-E which appears to be unrelated to the N-S polarity shown by the isotopic data. The isotopic data appears to reflect mantle mixing processes at depth involving both enriched and depleted mantle.

Lavecchia G & Stoppa F, *Journal of Volcanological and Geothermal Research*, 52, 277-293

MS10 : MOPm30 : G8

Wall-Rock Reaction, Decarbonation, and Carbonatite Eruption from the Upper Mantle

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Experimental simulations at upper mantle conditions show that carbonatite - wall-rock metasomatic reactions induced by infiltration result in wall-rock fracturing due to CO₂ liberation. Infiltration experiments were performed in a piston-cylinder apparatus at 1 GPa and 1000°C on couples where pre-synthesized harzburgite and Na-Ca carbonate melt were placed in contact. The couples were run vertically with melt on top for duration ranging between 0.5 and 24

hours. Polished sections of experimental samples were characterized by scanning electron microscope and electron microprobe. The major features are the presence of vein network in the infiltrated harzburgite, and of newly formed clinopyroxene at the expense of orthopyroxene. Major harzburgite invasion by carbonatite occurs through the vein network. Two clinopyroxene morphologies are found, one in the veins where orthopyroxene has been totally replaced, the other as rims around relict orthopyroxene. The second type could correspond to carbonatite wetting associated with porous flow. Both types illustrate the transformation of harzburgite (olivine + orthopyroxene) into wehrlite (olivine + clinopyroxene) and have been described in mantle xenoliths having experienced carbonatite-related metasomatism. The effect of CO₂ production has been estimated by calculating the volume increase associated with wall-rock reaction (decarbonation). These volume have in turn been converted into overpressure initiated at the locus of the reaction using CO₂ equation of state. In the case of the present experiments, the overpressure is of the order of 1 GPa. This figure is significantly higher than the threshold for tensile rock failure, therefore confirming that veins are caused by harzburgite reaction with carbonatite in the experimental samples. Applied to any mantle geotherm and using relevant metasomatic reaction involving carbonatites, volume computations yield the same result, i.e., wall-rock fracturing is expected. If gas expansion upon ascent and decompression is further taken into account, fractures extending several tens of kilometers can be produced in the mantle and can possibly breach to the surface provided that sufficient melt volumes (fractions of km³) are produced. This mechanism can explain explosive emplacement associated with dolomitic magmatism rooted in the mantle. Because of low abundance of carbon in the mantle, such magmatism should arise from sources anomalously rich in carbon. Such sources could be either regions where carbon was introduced by previous repeated metasomatic events involving carbon rich melts prior to major carbonatite magmatic event or regions where initial high carbon content is due to the survival of subducted carbonate-rich material.

MS10 : MOPm31 : G8

Transport of Mantle Carbon to the Crust and Surface by Carbonatitic Magmatism: Report of the ESF Workshop in the Kaiserstuhl Carbonatite Complex

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In connection with the EUG XI Symposium L6 "Mantle Carbon and the Carbon Cycle" a workshop with panel discussions is being held from 6-8 April in the Kaiserstuhl Alkaline Rocks-Carbonatite Complex, Rheingraben, Germany. Topics will include all the means by which carbon is brought by carbonatitic melts from the mantle to the crust and surface of the Earth. Focus of the discussions will be on evidences of carbonatites ascending directly from the mantle and their origins by melting of of carbonated mantle. Differences and distinctions between such primary carbonatites and higher level differentiation products are a key issue of carbonatite petrogenesis, so are the relationships between associated carbonate and silicate rocks, as in the Kaiserstuhl complex. Due to their quenched nature, extrusive carbonatites provide important constraints for the physical and compositional characterisation of carbonatitic melts. The Kaiserstuhl complex presents some highly informative examples of extrusive carbonatites. As a contribution to Symposium L6 the workshop summary and conclusions will be presented.

MS10 : MOPm32 : G8

Mantle Carbon Flux as Tested by Petroleum Reservoirs

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Some mantle carbon may reach higher crustal levels as a result of fluid migration through the lithosphere rather than as a result of volcanic or other igneous processes. Carbon dioxide occurrences in petroleum reservoirs provide samples for evaluating such a flux. Carbon dioxide is relatively common in petroleum reservoirs. But, although only just under 1 in 10 reservoirs contain <1% CO₂, just under 1 in 100 contain significant volumes (>20%) with the mean abundance being about 50% CO₂. Stable carbon isotope ratios suggest that where low volumes of CO₂ occur they

are derived from organic sources (δ¹³C values <-15‰). But in those reservoirs with large volumes the source of the CO₂ is from outside the petroleum system (δ¹³C values 0 to -10‰ and in a significant number of cases might be the mantle. A few specific studies using rare gas isotopes are beginning to test this idea in some cases substantiating a mantle origin but in at least one case not. A more general, global view will require further such case studies.

MS10 : MOPm33 : G8

Magma Degassing and Mixing in Oceanic Basaltic Volcanism: Carbon and Water Behaviour

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Concentration and isotopic features of submarine magmatic carbon and sometime water, are frequently, misinterpreted because they are taken at face value as representative of undegassed magma, whereas this is not always true for water and almost never for carbon. With the presently available precise calibration curves for water and carbon solubility, infrared absorptivities, isotopic fractionation curves for water-magma (D/H) and CO₂-magma (¹³C/¹²C), careful isotopic and concentration studies of coupled vesicle and dissolved water and carbon, make possible to reconstruct the magmatic evolution of these volatile species. Our studies of the Mid Atlantic Ridge (14°, 34° and 36°N), East Pacific Rise (12-21°N, 13°S, 23-26°S), Central, East and Southwest Indian Ridges, indeed display a wide variety of cases. However, one can recognize common degassing features and, also, very frequently the necessity of a magma mixing hypothesis.

Since water is a thousand to a hundred times more soluble than carbon in the range 0 to 10 kilobars, their partition between bubbles (vesicles) and magma (glass), is very different. The water vapour pressures vary between 2 and 50% of the total vesicle pressure depending on the eruption pressure and the initial water content.

The carbon isotopic composition of vesicles, the closer usually (but not equal) to the initial magma composition, varies in δ¹³C between -3 and -8‰, whereas the residual dissolved carbon varies between -4 and -21‰. The total carbon concentration varies between 30 and 4000 ppm (dissolved plus vesicles) whereas the dissolved part varies only between 30 and 130 ppm in the 200-500 bars range, reflecting super-saturation of less than 1 to 4 times.

Water contents vary widely, from 500 to 7000 ppm, and this variation cannot be explained by degassing, since, in the same pressure range, outgassing is not significant below a water content of about 5000 ppm. Water "lows" are particularly spectacular at the Rodriguez triple junction and in the Garrett Fracture Zone, whereas the 14°N site on the MAR displays virtually the total range of water concentrations on a 500 km fragment of the ridge.

A two steps degassing determines reasonable "magma chamber" depths between 0.5 and 6 km. However water results call inevitably for magma mixing.

Water-rich magmas (up to 1wt%) are vesicle-rich (e.g. popping rocks) or display δ¹³C in vesicle corresponding to degassing features. Consequently, they have been carbon-rich with initial carbon concentrations similar to water concentrations. On the contrary, water-poor magmas (500 to 2000 ppm) are vesicle-poor (<1vol%) and are sometime under-saturated at eruption.

All these results are interpreted as mixing of magmas extracted from different levels in the mantle with different volatile characteristics due to depletion of the mantle source as it rises toward the surface.

MS10 The Role of Mantle Carbon in the Global Carbon Cycle

MS10 : MOPm34 : G8

Origin of REE Mineralization in the Khibina and Vuoriyarvi Carbonatites (Kola, Russia) – Evidence from a C-O and Sr-Nd Isotope Study

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The high levels of REE and Sr in carbonatites provide a useful means of studying mantle source characteristics using Sr, Nd, C and O isotopes. The extreme compositions of REE-rich carbonatites are potentially particularly good for this, if disturbance from the subsolidus processes usually involved in forming REE-rich carbonatites can be ruled out.

The 370-380 Ma Khibina and Vuoriyarvi complexes on the Kola Peninsula, Russia, contain REE-rich carbonatite with burbankite ((Na,Ca)₂(Sr,Ba,Ce)₂(CO₃)₂) as the principal REE mineral. These burbankite-bearing carbonatites are thought to originate from a volatile-rich melt (Wall et al., 2000). During late-stage processes burbankite has been replaced in some rocks by various assemblages of REE-Sr-Ba minerals.

Within each complex the C-O and Sr-Nd isotopic data are similar for burbankite, co-existing calcite/dolomite and unmineralized carbonatites (Khibina: $\delta^{13}\text{C}(\text{PDB}) = -6.4$ - -5.8 ‰, $\delta^{18}\text{O}(\text{VSMOW}) = 7.3$ - 7.7 ‰, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}} = 0.70390$ - 0.70404 and $^{143}\text{Nd}/^{144}\text{Nd}_{\text{initial}} = 0.512305$ - 0.512314 , Vuoriyarvi: $\delta^{13}\text{C}(\text{PDB}) = -4.2$ - -3.0 ‰, $\delta^{18}\text{O} = 8.1$ - 9.4 ‰, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}} = 0.70313$ - 0.70315 and $^{143}\text{Nd}/^{144}\text{Nd}_{\text{initial}} = 0.512434$ - 0.512445). This indicates that the REE mineralization and their host carbonatites in each complex are derived from the same source and are co-genetic. There is, however, a great difference between the Sr, Nd and C isotopic signatures from Khibina and Vuoriyarvi, whereas the O values are similar. This suggests that the REE carbonatites of the two complexes originate from different isotopic sources. At least three mantle components are needed to explain variations in Sr and Nd compositions in the carbonatites from Kola. The high $\delta^{13}\text{C}$ values in Vuoriyarvi may be related to the presence of a crustal carbonate component, the low $\delta^{18}\text{O}$ values indicate that the crustal contamination occurred at high T and in the presence of an O-buffering silicate melt. Thus the high $\delta^{13}\text{C}$ observed can be attributed to subduction-related source contamination.

The burbankite alteration is an open-system hydrothermal process leading to multiple element transfer (Zaitsev et al., 1998). It has produced pseudomorphous mineral assemblages after burbankite which are characterized by high $\delta^{18}\text{O}$ values compared with primary burbankite. In one of the Khibina samples it is also accompanied by a positive $\delta^{13}\text{C}$ shift. Co-existing calcite and dolomite have retained their original C and O isotope compositions, and one calcite sample from Khibina shows strong positive $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ shifts similar to those of the pseudomorph. The high $\delta^{18}\text{O}$ and sometimes high $\delta^{13}\text{C}$ values can be attributed to low temperature fluid-mineral isotope exchange taking place during and/or after crystallization as usually observed in carbonatites (Deines, 1989).

The Sr and Nd isotope compositions of pseudomorphs and associated calcite/dolomite in general are identical to those of burbankite and associated carbonates suggesting that the fluids which caused burbankite alteration are from the same source, i.e. carbonatitic. Small variations in the Sr and Nd isotope signatures point to interaction of the pseudomorph-forming fluid with alkali silicate wall rocks.

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