REDUCED CARBONACEOUS MATTER IN BASALTS AND MANTLE XENOLITHS.

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Crack surfaces and grain boundaries in many basalts and mantle xenoliths display a peculiar bluish purple discoloration or iridescence that suggests the presence of a thin film. C x-ray mapping and x-ray photoelectron spectroscopy (XPS) indicate that such iridescent surfaces possess a thin film of amorphous C a few nm thick (Mathez and Delaney, 1981; Mathez, 1987; Tingle et al., 1990; 1991). C in the films is predominantly C-C and/or C-H bonded species with smaller amounts of various C-O bonded species. Less commonly, carbonaceous particles up to 20 μm across are present on crack surfaces in some xenoliths. Carbonaceous matter (films and particles) contains minor quantities of Si, Al, alkalis, halogens, transition metals, N, O and sometimes organic compounds (mostly hydrocarbons). With the exception of organics, these are components expected to be present in volcanic gas, and the crack surfaces on which carbonaceous films occur probably are produced by thermal stresses during eruption and cooling of the basaltic lava and attendant xenoliths. Mathez (1987) and Tingle et al. (1990;. 1991) have postulated that carbonaceous films are produced by heterogeneous surface reactions involving volcanic gas and fresh, chemically active crack surfaces. Indeed, we have produced carbonaceous films, similar in thickness and C speciation to those observed in natural rocks, in laboratory experiments simulating the volcanic environment.

Carbonaceous matter on crack surfaces has been observed in a variety of samples from different geologic environments. These include basalts and peridotite xenoliths from the 1801 AD flow of Hualalai Volcano, Hawaii, San Carlos and Kilbourne Hole, Arizona, basalts from the Kilauea east rift and the Mid-Atlantic Ridge, megacrysts (garnet and diopside) from the Jagersfontein kimberlite, and gabbros from the Pt-group element mineralized zones of the Bushveld and Stillwater layered igneous complexes. The chemistry of this carbonaceous matter shows considerable variation among samples from different localities and even among samples from the same locality.

Organic compounds associated with carbonaceous films have been detected by very sensitive thermal desorption photoionization mass spectrometry in some samples (Tingle et al., 1990; 1991). They are desorbed at temperatures of 300-700°C and consist principally of compounds with molecular weights less than 150 amu (mostly alkanes, alkenes and aromatics with lesser amounts of N- and O-bearing compounds and sulfur species). That temperatures in excess of 300°C are required to desorb organic material suggests that the observed species are pyrolysis products of more complex compounds or that the low molecular weight species must be physically or chemically bound in the carbonaceous material. It has been shown that organic matter, when present, is not laboratory or instrument contamination, environmental biogenic matter incorporated during residence at the Earth's surface, or pyrolized biogenic matter incorporated by the lava advancing over vegetation during eruption. Not all samples with carbonaceous films contain organics. For example, organics were detected in only 3 of 5 xenoliths analyzed from Hualalai, and organic compounds were not detected in any of the Stillwater and Bushveld samples. Tingle et al. (1990) have suggested that 10-50% of the total C in the San Carlos olivine films may be organic, although estimates of the organic abundance or even relative amounts of organic versus amorphous C are subject to some uncertainties.

The organic matter associated with carbonaceous films has two possible sources. Organic compounds may have been produced by Fisher-Tropsch-like catalytic reactions at the mineral-gas interface. Alternatively, organic compounds may have been assimilated into the volcanic gas prior to eruption and then deposited on crack surfaces during C film formation. The small amount of organic matter generally present is not sufficient to determine its origin. As pointed out by Tingle et al. (1990, and references contained therein), on the one hand, biogenic matter (low molecular weight hydrocarbons and biomolecules, steranes and terpanes) has been identified in volcanic emanations, hydrothermal fluids, and steam from geothermal fields. On the other hand, abiogenic

synthesis of a diverse suite of organic compounds has been achieved in meteorites (carbonaceous chondrites) in the solar nebula and in laboratory experiments, although silicates are not generally regarded as the substrates on which organic synthesis reactions occurred. Also, methane and light hydrocarbons in hydrothermal fluids of the East Pacific Rise and Mid-Atlantic Ridge are abiogenic, although the mechanisms by which they are produced are not well understood. Also, hydrocarbons in fluid inclusions in rocks of the Khibiny and Ilimaussaq alkaline intrusions are demonstrably abiogenic. We believe the present data favor an abiogenic synthesis, although a biogenic origin cannot be dismissed at this time.

The isotopic composition ($\delta^{13}C$) of C in films on iridescent crack surfaces in San Carlos olivine was determined by stepped combustion techniques to be -32‰ (D. P. Mattey and T. N. Tingle, 1991, manuscript in preparation), suggesting that there is a strong fractionation of C isotopes during C film formation. Even if 50% of the crack-situated C in the San Carlos olivine is assimilated biogenic matter with $\delta^{13}C$ = -50‰, the $\delta^{13}C$ of C films deposited by the volcanic gas on fresh crack surfaces would be -14‰, which is considerably more depleted than the -5 to -8‰ typically observed for CO_2 in basaltic gases.

To further investigate the formation of carbonaceous films and the possible abiogenic synthesis of organic matter during eruption and cooling of basaltic magma, we have exposed freshly cleaved {010} surfaces of San Carlos olivine to C-O-H gases at 400-800°C. Two gas compositions were employed: $2CO_2 + 2H_2O + H_2$ and $2CO_2 + H_2$ derived from decomposition of oxalic acid dihydrate and oxalic acid, respectively. In one set of experiments, gem-quality single crystals were loaded in air with a small amount of oxalic acid and welded shut; the samples were heated to 800°C and quenched in liquid nitrogen to produce cracks. In a second set of experiments, large single crystals were cleaved in an argon glove bag and loaded into Au tubes with oxalic acid, hermetically sealed and then welded shut. Samples were then heated to 400-800°C for 2-30 min to allow for heterogeneous reactions between the mineral surface and gas phase to occur.

Carbonaceous films were produced in all samples, but none of them contained any detectable organic material. Films attained thicknesses comparable to those observed in natural samples. The speciation of C in films was dependent on the gas composition and $f(O_2)$. Films produced at relatively oxidizing conditions resembled those observed in natural samples, in that the prominent species observed were C-C/C-H with lesser amounts of C-O bonding; films produced at the more reduced conditions consisted of roughly equal amounts of carbide, C-C/C-H, and C-O species. Scanning electron microscopy has not revealed any crystallites or particles on these surfaces. It is important to note that thermodynamic calculations for these two sets of experiments do not predict graphite, carbides, carbonates, or hydrocarbons to be stable phases. Similarly for natural samples, the chemical environment during eruption is much too oxidizing for graphite (and presumably amorphous C) and hydrocarbons to be stable phases. These experiments suggest that the nature of fresh crack surfaces is such that they can stabilize amorphous C and hydrocarbons in a cooling lava.

The study of carbonaceous matter has several implications. First, the low-temperature (400-700°C) isotopically light (-26‰) C released by stepped heating techniques from basalts and xenoliths (Mattey, 1988) is not all contamination as was previously thought; part of the low-temperature C is due to carbonaceous films on crack surfaces, grain boundaries, and vesicle and fluid inclusion walls. In their measurement of the $\delta^{13}C$ of carbonaceous films in San Carlos olivine, Mattey and Tingle (1991, manuscript in preparation) found that approximately 50% of the C analyzed below 800°C was due to C films, 10% was due to adventitious C contamination of olivine surfaces, and 40% was instrument contamination.

Second, the apparent fractionation of C isotopes between CO_2 vapor and CO_2 dissolved in basalt melt indicated by the "popping rocks" of the Mid-Atlantic ridge (Pineau et al., 1976) and the later experiments of Javoy et al. (1978) may be explained by the presence of isotopically depleted C films on vesicle walls and cracks in the popping rocks and experimental glasses. The vapor-melt C isotopic fractionation is expected to be close to that of CO_2-calcite (because C dissolves in basalt melt as CO_3^{2-} species) at magmatic temperatures (1-2‰), and the recent experimental results of Mattey et al. (1990) support this. The mantle C flux of 0.6-7.2 x 10^{14} g/yr calculated assuming a 4‰ fractionation (Javoy et al., 1982) must be reconsidered, and with it the hypothesis that C must be subducted in order to explain the modern mantle C flux.

There are several lines of evidence to suggest that C is indeed subducted, but most of that will be carbonates in pelagic sediment and altered oceanic crust with $\delta^{13}C \approx 0‰$, and a much smaller amount will be kerogen with very depleted $\delta^{13}C$. Thermal models of subduction zones and carbonate phase equilibria predict that carbonates, in general, will not decompose during subduction. However, the vast majority of CO_2 coming out of the Earth today has a very uniform $\delta^{13}C = -5$ to $-8‰$. It seems to us that the $-5‰$ $\delta^{13}C$ of the modern mantle is best explained by a primordial C source (of approximately the same isotopic composition) that was stable during accretion and differentiation. That such a C reservoir might exist in a planetary core is suggested by the presence of graphite in iron meteorites, and $\delta^{13}C$ of such graphite is -5 to $-8‰$ (Deines and Wickman, 1975). At present, the best evidence of C recycled by subduction appears to be diamonds of eclogitic paragenesis with depleted $\delta^{13}C$ (Kirkley and Gurney, 1989).

REFERENCES

Deines, P. and Wickman, F. E. (1975) A contribution to the stable carbon isotope geochemistry of iron meteorites. Geochimica Cosmochimica Acta, 39, 547-557.

Javoy, M., Pineau, F., and Ilyama, I. (1978) Experimental determination of the isotopic fractionation between gaseous CO_2 and carbon dissolved in tholeiitic magma: A preliminary study. Contributions to Mineralogy and Petrology, 67, 35-39.

Kirkley, M. B., and Gurney, J. J. (1989) Carbon isotope modelling of biogenic origins for carbon in eclogitic diamonds. Workshop on Diamonds, 28th Int. Geol. Congress, Washington, D. C.

Mathez, E. A. (1987) Carbonaceous matter in mantle xenoliths: Composition and relevance to the isotopes. Geochimica Cosmochimica Acta, 51, 2339-2347.

Mathez, E. A., and Delaney, J. R. (1981) The nature and distribution of carbon in submarine basalts and peridotite nodules. Earth and Planetary Science Letters, 56, 217-232.

Mattey, D. P. (1988) Carbon isotopes in the mantle. Terra Cognita, 7, 31-37.

Mattey, D. P., Taylor, W. R., Green, D. H., and Pilinger, C. T. (1990) Carbon isotopic fractionation between CO_2 vapour, silicate and carbonate melts: An experimental study to 30 kbar. Contributions to Mineralogy and Petrology, 104, 492-501.

Pineau, F., Javoy M., and Bottinga, Y. (1976) $^{13}C/^{12}C$ ratios of rocks and inclusions in popping rocks of the Mid-Atlantic Ridge: Their bearing on the problem of isotopic composition of deep-seated carbon. Earth and Planetary Science Letters, 29, 413-421.

Tingle, T. N., Hochella, M. F., Becker, C. H., and Malhotra R. (1990) Organic compounds on crack surfaces in olivine from San Carlos, Arizona and Hualalai Volcano, Hawaii. Geochimica Cosmochimica Acta, 54, 477-485.

Tingle, T. N., Hochella, M. F. and Mathez, E. A. (1991) Carbonaceous matter in peridotites and basalts studied by XPS, SALI and LEED. Geochimica Cosmochimica Acta, 55, (in press).