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Carbon dioxide in magmas and implications for hydrothermal systems

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Abstract This review focuses on the solubility, origin, abundance, and degassing of carbon dioxide (CO₂) in magma–hydrothermal systems, with applications for those workers interested in intrusion-related deposits of gold and other metals. The solubility of CO₂ increases with pressure and magma alkalinity. Its solubility is low relative to that of H₂O, so that fluids exsolved deep in the crust tend to have high CO₂/H₂O compared with fluids evolved closer to the surface. Similarly, CO₂/H₂O will typically decrease during progressive decompression- or crystallization-induced degassing. The temperature dependence of solubility is a function of the speciation of CO₂, which dissolves in molecular form in rhyolites (retrograde temperature solubility), but exists as dissolved carbonate groups in basalts (prograde). Magnesite and dolomite are stable under a relatively wide range of mantle conditions, but melt just above the solidus, thereby contributing CO₂ to mantle magmas. Graphite, diamond, and a free CO₂-bearing fluid may be the primary carbon-bearing phases in other mantle source regions. Growing evidence suggests that most CO₂ is contributed to arc magmas via recycling of subducted oceanic crust and its overlying sediment blanket. Additional carbon can be added to magmas during magma–wallrock interactions in the crust. Studies of fluid and melt inclusions from intrusive and extrusive igneous rocks yield ample evidence that many magmas are vapor saturated as deep as the mid crust (10–15 km) and that CO₂ is an appreciable part of the exsolved vapor. Such is the case in both basaltic and some silicic magmas. Under most conditions, the presence of a CO₂-bearing vapor does not hinder, and in fact may promote, the ascent and eruption of the host magma. Carbonic fluids are poorly miscible with aqueous fluids, particularly at high temperature and low pressure, so that the

presence of CO₂ can induce immiscibility both within the magmatic volatile phase and in hydrothermal systems. Because some metals, including gold, can be more volatile in vapor phases than coexisting liquids, the presence of CO₂ may indirectly aid the process of metallogenesis by inducing phase separation.

Introduction

After H₂O, carbon dioxide is the second most common gas in volcanic exhalations (White and Waring 1963; Symonds et al. 1994). In gases exsolved from basaltic magmas, CO₂ sometimes exceeds water in concentration (e.g., Gerlach 1980; Giggenbach 1997), presumably due to its greater abundance in some mantle source regions. The presence of CO₂ in magmatic systems, combined with its relatively low solubility, results in early exsolution of vapors that are rich in CO₂ (Holloway 1976). Once exsolved, this low density vapor phase has important implications for the ascent and eruption of CO₂-bearing magmas (Papale and Polacci 1999). Many workers have noted evidence for CO₂-rich fluids in a variety of intrusion-related ore deposits, particularly those associated with Au and lithophile enrichment (Newberry et al. 1995; Goldfarb et al. 1998; Thompson et al. 1999). In such systems, CO₂ may be derived from the magma, and even from a mantle source, although there are other means for CO₂ to enter ore-forming systems such as decarbonation reactions in wallrock and dissolution of CO₂ and carbonate minerals from crustal hydrothermal systems.

This review focuses on CO₂ in magmas, providing an introduction to the behavior of CO₂-bearing vapors within magmas, and as they enter hydrothermal systems. First, it outlines current knowledge about the solubility of carbon species in silicate melts, then continues with a summary of carbon in the mantle and mantle melts, and proceeds to discuss CO₂ in intermediate and silicic magmas. Next, it concentrates on

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the composition of exsolved magmatic vapors and the effect of CO₂ on magma properties, ascent, eruption, and intrusion. Finally, it provides a brief summary of CO₂ in hydrothermal and geothermal systems, and speculates on the importance of CO₂ in some ore-forming systems. This synthesis of current knowledge about CO₂, and its role in magmas, attempts to provide economic geologists with a background that can be used when interpreting the role of CO₂ in intrusion-related deposits.

The solubility of CO₂ in silicate melts

CO₂ dissolution

To understand the systematics of CO₂ behavior in igneous systems, one must first consider how CO₂ dissolves in magmas and the variables that influence its solubility (see Blank and Brooker 1994 for an excellent review). Experimental studies in the 1960s and 1970s recognized that CO₂ solubility in natural rock melts is about an order of magnitude less than that of water (e.g., Wyllie and Tuttle 1959; Kadik et al. 1972). In the late 1970s and 1980s, experimentalists were able to use vibrational spectroscopy to determine the speciation of volatiles within silicate melts and obtain more quantitative solubility estimates. Mysen et al. (1975) used ¹⁴C beta-track mapping techniques to study the solubility of CO₂ in a variety of natural melt compositions and found that it dissolves both as carbonate groups and molecular CO₂. Later, Fine and Stolper (1985) explored the incorporation of CO₂ in sodium aluminosilicate glasses, and found that it dissolved both as molecular CO₂ and Na–CO₃ ionic complexes, with the latter increasing along with Na₂O on the Na₂O–SiO₂ join. In subsequent studies, researchers have found that CO₂ dissolves solely as carbonate groups in basaltic melts including mafic alkaline magmas such as basanites, leucitites, and nephelinites (Blank and Brooker 1994). In contrast, solely molecular CO₂ is found in rhyolites (Fogel and Rutherford 1990). Intermediate melt compositions (andesites) have both species present (Mysen et al. 1975; King et al. 1996), as is the case for evolved silica-undersaturated magmas such as phonolites (Blank and Brooker 1994).

Because CO₂ reacts with the melt as it dissolves to form carbonate groups in mafic melts, its solubility is highly dependent on the nature and abundance of various cations; in particular, Ca, K, and Na. As a result, carbonate is far more soluble in alkaline basalts than tholeiites (Blank and Brooker 1994). Dixon (1997) derived a parameter (Π), which she used to model the relationship between carbonate solubility and melt composition for tholeiitic to leucititic compositions. The variable Π , which correlates positively with carbonate solubility, decreases as a function of silica and alumina concentrations. It also increases with alkalis and alkaline earth elements (and therefore with non-bridging oxy-

gens). She found that the effect of Ca²⁺ was most pronounced, followed by K⁺, Na⁺, Mg²⁺, and Fe²⁺ in descending order of importance. In contrast, CO₂ does not react with the melt as it dissolves in molecular form, so that there should be little variation in CO₂ solubility in felsic magmas. Moreover, on a molar basis, CO₂ solubility changes little with melt composition along the tholeiitic basalt–rhyolite join (Blank and Brooker 1994; see also Fig. 1).

Solubility as a function of pressure and temperature

In all studied magma types, the solubility of CO₂ increases with pressure at a nearly linear rate (Fig. 1). Temperature effects are not so simple, as they are dependent on the mechanism of incorporation of the CO₂ in the melt (Stolper et al. 1987). In rhyolitic magmas, the solubility of CO₂ clearly decreases as temperature increases (see Fig. 4 from Fogel and Rutherford 1990). This is consistent with the typical inverse correlation between molecular gas solubility and temperature, whether in room-temperature liquids, hydrothermal fluids, or rock melts. Exceptions occur when the gases dissolve by interacting with the melt to form charged complexes (Fig. 2). For example, the solubility of sulfate (which exists only in oxidized magmas) increases with temperature (Baker and Rutherford 1996), as does carbonate solubility in albite melts (Stolper et al. 1987) and basaltic melts (Mysen et al. 1975). In general, though, the temperature effect on solubility is very small compared with the effects of melt composition and pressure (Blank and Brooker 1994).

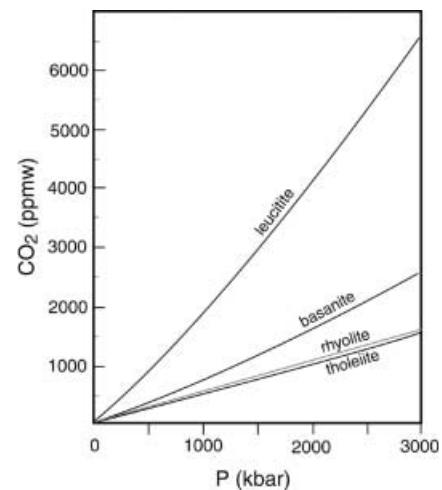


Fig. 1 Solubility of total CO₂ (molecular + carbonate) as a function of pressure for four melt compositions (ppmw parts per million by weight). Leucitite, basanite, and tholeiitic basalt calculated from compositions and parameters given in Holloway and Blank (1994) at 1,200 °C. Rhyolite curve from experimental data of Fogel and Rutherford (1990) at 1,150 °C. The solubility of CO₂ in rhyolite and tholeiitic basalt are very similar. The CO₂ solubility increases both with pressure and with magma alkalinity

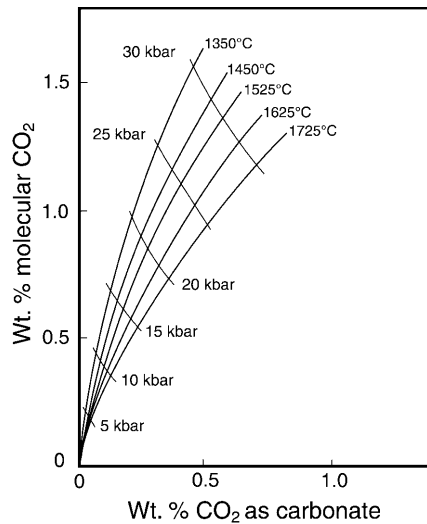


Fig. 2 Molecular CO₂ vs. carbonate concentrations for CO₂-saturated albite melt (after Stolper et al. 1987). In albite, CO₂ dissolves as both carbonate and molecular CO₂. Bulk solubility increases with pressure. The carbonate to molecular CO₂ ratio increases sympathetically with temperature

Solubility as a function of the presence of other volatiles

Blank et al. (1993) showed that Henry's Law applies for the H₂O–CO₂–rhyolite system at pressures < 1 kbar and magmatic temperatures. In a melt–vapor system where the vapor contains two components (in this case CO₂ and H₂O), addition of one gas dilutes the other gas, decreasing its activity and consequently decreasing its concentration (solubility) in the melt. In other words, addition of water to a melt–CO₂ system will decrease the solubility of CO₂. In such a case, Henry's Law holds for the melt, and the activity of a constituent is proportional to its concentration, which is decreased by addition of another component. This concept is illustrated in Fig. 3, where the solubility of CO₂ at fixed temperature and pressure varies with vapor composition in the H₂O–CO₂–melt system. There is some controversy whether this Henrian behavior in the melt continues at high pressures (> 5 kbar; e.g., Mysen et al. 1975) due to the possible depolymerizing effect of water on the melt structure (cf. Stolper et al. 1987).

CO₂ in the mantle

The first introduction of CO₂ into mafic magmas occurs during partial melting of the mantle. The presence of mantle-derived carbon is most obviously associated with continental and oceanic rifts where deep melting events create carbon-rich, silica-undersaturated magmas. Bailey and colleagues (e.g., Bailey 1987; Bailey and Macdonald 1987; Bailey and Hampton 1990) have repeatedly argued that tectonic rift zones are accompanied by unusually carbon-rich magmas, as corroborated by gas-rich groundwaters, CO₂-rich volcanic gases, and the associ-

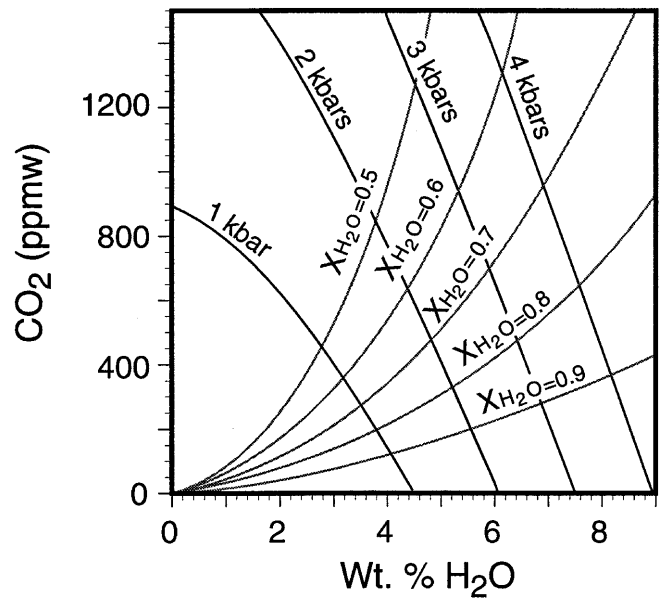
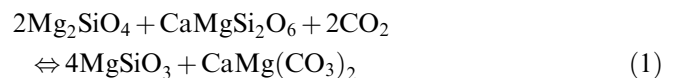


Fig. 3 Solubility plot for system rhyolite–H₂O–CO₂ at 675 °C. Lines labeled with units of pressure represent isobars that display solubility of H₂O and CO₂ as function of fluid composition; intersections with X- and Y-axes represent H₂O and CO₂ solubility, respectively – all other points being mixtures. Isopleths labeled with units of X_{H₂O} display the composition of vapor in equilibrium with the melt. Melt compositions (as deduced from silicate melt inclusions, fluid inclusions, etc.) can be plotted to calculate the minimum pressure at which the melt would be saturated with a vapor phase (saturation pressure). The corresponding isopleth would indicate the composition of vapor that would exsolve

ation of rifts with unusual magma compositions (carbonatites and strongly silica-undersaturated magmas such as nephelinites and melilitites). Except when created at unusually deep mantle depths where diamond is stable (Fig. 4; see Haggerty 1999), such magmas will most typically be created due to melting of carbonated mantle.

Wyllie and Huang (1976) showed that the reaction:



is favored at mantle pressures (Fig. 4). At pressures > 28 kbar (Olafsson and Eggler 1983), magnesite (MgCO₃) is the stable crystalline carbonate phase, even in iron-bearing compositions (Dalton and Wood 1993). The carbonate-forming reactions destabilize the calcium-rich (cpx) and silica-poor minerals (olivine) within the mantle. Therefore, when lherzolite is melted, resulting liquids are rich in calcium and magnesium and are low in silica, as is observed in silica-undersaturated magmas (nephelinites, melilitites), carbonatites, and kimberlites – all magma types commonly associated with high abundances of CO₂ (Brey 1978). Later experimental studies have shown that solid carbonates should be present in mantle peridotites at temperatures below 1,200 °C and at oxidation states above QFM (the quartz–fayalite–magnetite buffer) minus 0.5 (Dalton and Wood 1995).

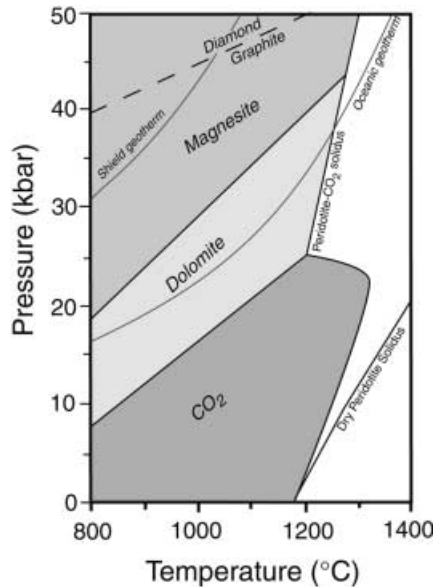


Fig. 4 Stability of carbonic phases in lherzolitic mantle (the CaO–MgO–SiO₂–CO₂ system). The CO₂, dolomite, and magnesite fields are after Dalton and Wood (1993), with peridotite–CO₂ and peridotite–dry solidus from Wyllie (1978). Shield and oceanic geotherms from Bailey (1985). Note that both the shield and oceanic geotherms would pass through the field of carbonated mantle provided that the mantle f_{O_2} is sufficiently high to stabilize carbonate (i.e., >QFM minus 0.5; Dalton and Wood 1995)

Although melting will tend to deplete the mantle with respect to carbon, there are a number of processes that can lead to subsequent enrichment in volatiles. Studies of mantle xenoliths, particularly those erupted with alkali basalts, indicate that the mantle can undergo metasomatism by trace element enriched fluids or melts (e.g., Bailey 1987; Menzies and Hawkesworth 1987; Stolz and Davies 1988). In many cases, the fluid responsible for these changes is interpreted to be CO₂-rich, based on the presence of CO₂-rich fluid inclusions and reaction assemblages (Dautria et al. 1992). Carbonated melts have been documented in peridotite nodules from the Kerguelen Islands by Schiano et al. (1994), who found carbonate-rich melt inclusions and concluded that they represented metasomatic liquids.

Evidence for carbonate mineral phases within mantle peridotite nodules was first documented by McGetchin and Besancon (1973), who found small carbonate inclusions within pyropes. Amundsen et al. (1987) later described quenched carbonate-bearing melts within spinel peridotite xenoliths from Spitsbergen. Later studies on these samples by Ionov et al. (1993) identified magnesium-rich dolomites, implying equilibrium with mantle minerals. Most of the carbonate minerals in these rocks showed evidence for breakdown by reaction with peridotite. Such breakdown should be common and the preservation of any relict mantle carbonate minerals is likely to be extremely rare. Canil (1990) found that Eq. (1) is readily reversed at magmatic temperatures and sub-mantle pressures. In his experiments, synthetic per-

idotites were held at 1,000 °C and decompressed at rates equivalent to 90 km/h prior to rapid quenching; yet in all cases the dolomite broke down completely. Berg (1986) described calcite–brucite intergrowths, which may also represent relict mantle carbonate phases that did not survive their ascent to the surface. Given such rapid breakdown, it is not surprising that mineralogical evidence for the host phase for CO₂ in the mantle is quite rare. Typically, such evidence consists of either remnant carbonate melts or carbonate inclusions within rigid crystal hosts.

In mantle with lower oxidation states or higher temperatures, carbon is likely to be present either in a fluid phase, as diamond (at > 50 kbar), or as graphite. Holloway (1998) presented a model for production of mid-ocean-ridge basalt from a graphite-saturated mantle under relatively reducing conditions. At low pressures, carbonate minerals are not stable and will react to form CO₂ vapor. Roedder (1965) showed convincing evidence for nearly pure-phase CO₂ vapor exsolved in the deep crystallization environment of numerous basaltic magmas. Of 72 occurrences of olivine-bearing nodules found in basalt lavas, 64 contained high-density CO₂-dominated fluid inclusions that must have been trapped at depths of 10–15 km. Many olivine phenocrysts from the host lavas also contained similar inclusions, indicating that the magmas were saturated at great depth with CO₂-rich fluids.

Estimates of CO₂ concentrations in magmas

Evidence for the presence of CO₂ in crustal magmas is not limited to inclusions in mantle and cognate xenoliths. During the past 20 years, experimental and petrologic studies of igneous volatiles have led to a far greater understanding of the abundance of dissolved and exsolved gases in magmatic systems. Although concentrations of CO₂ in silicate glasses had been estimated by techniques such as ¹⁴C beta-track counting and manometric techniques, it was not until Fourier transform infrared (FTIR) spectroscopy became widely used that quantitative techniques for measurement of CO₂ concentrations were developed (Fine and Stolper 1985; Stolper et al. 1987). Subsequently, studies of experimental run products, quenched natural glasses and silicate melt inclusions were begun (Dixon et al. 1988; Newman et al. 1988; Anderson et al. 1989; Fogel and Rutherford 1990). The latter are small blebs of silicate melt (often quenched to glass) that are trapped in phenocryst hosts during pre-eruptive crystallization. Assuming no post-entrapment processes have changed the melt inclusion composition (see Lowenstern 1995), these features provide information on the melt composition and dissolved volatiles at the time of trapping. In this section, I review the recent literature on measured CO₂ concentrations in natural melts, and what has been learned about the nature and abundance of CO₂-bearing igneous fluids in the middle to upper crust.

Alkalic basalts

Given the apparent presence of solid carbonates, CO₂-bearing fluid, and graphite in different parts of the mantle, magma generation will result in CO₂-bearing liquids. For example, carbonate is the first mineral phase to melt when the peridotite solidus is exceeded at 40 kbar (Canil and Scarfe 1990) and this would also be expected at lower pressures (Fig. 4). The CO₂ concentrations in partial melts from carbonate-bearing mantle peridotite will be dependent on its bulk carbonate content and the extent of melting. In many cases, initial partial melts might be extremely carbon rich, but would be diluted as melting proceeded. Such a trend was recently observed by Dixon et al. (1997), who looked at dissolved CO₂, both measured and calculated, for a range of basalt compositions from the submarine North Arch volcanic field, north of Oahu (Hawaii). They argue that a homogeneous mantle source was variably melted (1.6–9.0% batch melting), producing liquids ranging with progressive melting from nephelinite to basanite to alkaline olivine basalt (AOB). Initial volatile contents were assumed to correlate with P₂O₅ and were calculated to range from 6.9 wt% CO₂+H₂O in the nephelinites to 1.8 wt% in the AOBs (with CO₂/H₂O by wt=2.5 in both). The mantle source region was inferred to be fluid absent, although the host phase for carbon was not stated and batch melting was assumed. The volatile content of the unmelted source mantle was estimated to be 525±75 ppmw (ppm by weight) H₂O and 1,300±800 ppmw CO₂. Upon ascent, the magmas would not have begun degassing (i.e., reached their saturation pressures) until reaching depths of 25–40 km, two to three times shallower than their source region. Matrix glass in lavas dredged from the seafloor at ~4 km depth had degassed, but the bulk rocks still contained several wt% total volatiles due to the abundance of CO₂-rich vesicles, consistent with the high calculated volatile contents. Similar results were found by Moore et al. (1977), who discovered that vesicles in a variety of submarine basalts contained more than 95% CO₂, requiring saturation with CO₂ at water depths of 5 km and greater.

The highest dissolved CO₂ contents measured in natural glasses come from silicate melt (glass) inclusions in olivine from mafic basalts. Because the inclusions are often trapped at great pressure (several kbar), these melts have degassed far less than basalts emplaced at depths of 3 to 4 km below sea level (0.3–0.4 kbar). Marianelli et al. (1999) analyzed glass inclusions in potassium-rich tephrites from Vesuvius, Italy, that have as much as 3 wt% dissolved H₂O and 0.3 wt% dissolved CO₂, requiring saturation with a volatile phase at pressures up to and over 5 kbar. These magmas fed a shallow magma chamber at a depth of 1–2 km, where they degassed and crystallized to form a potassium-rich phonotephrite with very low dissolved CO₂ (< 500 ppmw) and less than 1 wt% dissolved H₂O. Similarly, Eschenbacher et al. (1998) studied alkalic

magmas from Mt. Erebus, Antarctica, which ranged in composition from basanite through evolved phonolites. They found very high dissolved CO₂ concentrations in melt inclusions trapped within olivine phenocrysts; as much as 0.7 wt%, corresponding to saturation pressures of 3–4 kbar given the measured H₂O concentrations of 1.15–1.75 wt%. As in the Vesuvius magmas, evolved magmas related to the deep mafic melts are depleted in volatiles, reflecting crystallization and chemical evolution in a shallow magma chamber where CO₂, H₂O, and S are lost to the atmosphere and/or overlying hydrothermal system. Eschenbacher et al. (1998) conclude that volatile saturation and degassing occurs throughout the continuous fractionation from basanite through phonolite.

MORB and ocean island basalts

A large amount of work has been done on volatile concentrations in MORB glasses dredged from the ocean floor. Johnson et al. (1994) review some of the pertinent literature and describe the analytical difficulties of volatile analysis in bulk glass samples. In general, MORB glasses are H₂O-undersaturated, but contain vesicles, requiring saturation with a CO₂-rich gas at the depth of emplacement. Concentrations of CO₂ are higher for bulk manometric analyses than for spot analyses (e.g., FTIR spectroscopy), presumably because they are affected by the presence of CO₂ in vesicles (Moore et al. 1977). In a study of lavas with numerous CO₂-rich bubbles (“popping rocks”), Pineau and Javoy (1983) showed that the difference between the carbon isotopic composition of CO₂ from vesicles and CO₂ dissolved in MORB glass could be attributed to isotopic fractionation due to outgassing during ascent and that the magnitude of fractionation implied CO₂ concentrations of 0.2 to 1.0 wt% in the mantle source region. In general, H₂O concentrations in MORBs correlate with K₂O, and are interpreted to track the degree of melting in the source region. The CO₂ does not correlate with major or trace elements, presumably due to the effect of degassing (Johnson et al. 1994).

Estimates of initial dissolved CO₂ concentrations in parental Kilauean ocean island basalts (Hawaii) range from a minimum of 0.2 wt% (Anderson and Brown 1993) to 0.3 wt% (Greenland et al. 1985) to 0.6 wt% (Gerlach and Graeber 1985). Anderson and Brown (1993) estimated saturation pressures for melts in Kilauean glass inclusions that ranged up to 5 kbar, although most crystals appeared to grow at much lower pressures. The 5 kbar estimate is consistent with the data of Roedder (1965), who found CO₂-dominated fluid inclusions in both olivine phenocrysts and cumulate xenoliths, requiring saturation with a CO₂-rich vapor phase at depth. At Reunion Island, Bureau et al. (1998) interpreted fluid and melt inclusion compositions to imply that magmas were volatile-saturated with a CO₂-rich fluid at pressures of at least 5 kbar.

Arc basalts and andesites

Recently, several studies have explored the dissolved CO₂ concentrations within mafic arc magmas. Sisson and Bronto (1998) worked on high-magnesium basalts from the 1983 eruption of Galunggung, on the volcanic front in Java, Indonesia. They found low H₂O concentrations (0.21 to 0.38 wt%) in olivine-hosted melt inclusions, but elevated CO₂ (as much as 750 ppmw) and S (as much as 2,200 ppmw), indicating that the inclusions had not leaked and were instead trapped during ascent through the crust at depths of 3 to 6 km. Presumably, the magmas were saturated with a CO₂-dominated vapor during much of their ascent through the crust, although the inclusions were trapped at low pressure, after much degassing occurred. Sisson and Bronto (1998) argue that the high-magnesium basalt was created by upwelling and pressure-release melting of the mantle wedge, without significant input from fluids and magmas derived from the subducted slab. This accounts for the extremely water-depleted nature of the magma, which would be unexpected for basalts incorporating slab-derived fluids.

Such a slab-influenced melt was studied by Roggen-sack et al. (1997), who found that basaltic melt inclusions from Cerro Negro (Nicaragua) had elevated concentrations of dissolved H₂O (as much as 6 wt%) and CO₂ (some > 1,000 ppmw), yielding estimated saturation pressures as high as 6 kbar (i.e., ~21 km). Studied basalts that erupted explosively in 1992 are interpreted to have stagnated and crystallized at greater depths than those that erupted effusively three years later. The high CO₂ (and H₂O) flux from arc magmas with a significant slab component is consistent with the conclusions of Sano and Williams (1996), who estimated that only about 10% of the CO₂ degassed from subduction-zone volcanoes was derived from the mantle and that a major part of the CO₂ flux was recycled from the subducted oceanic crust and its overlying sediments. Because subduction zones produce almost two thirds of the volcanogenic carbon flux, crustal recycling represents a major source of carbon to the atmosphere (Sano and Williams 1996; Alt and Teagle 1999). Similarly, Giggenbach (1996) asserted that the volatile budget of arcs follows a steady state, whereby a major part of the CO₂ and N₂ flux is recycled via breakdown of sediments from the subducted slab and these gases return to the surface through arc volcanism. Presumably, much of the recycled carbon comes from carbonaceous sediments and ooze, and marine limestone (Wyllie and Huang 1976; Plank and Langmuir 1993; Alt and Teagle 1999), given that carbonate phases subducted with basalt are likely to break down at low pressures (Canil and Scarfe 1990), before they can reach the depth of magma generation.

Silicic magmas

Although rhyolitic and dacitic magmas are often assumed to contain only H₂O-rich gas, many studies have

found evidence for appreciable CO₂. Using infrared (FTIR) spectroscopy, Newman et al. (1988) undertook the first study to quantify the abundances of both CO₂ and H₂O dissolved in natural silicic glasses. Analyzing quenched obsidian fragments ejected from the throat of the Mono Craters (California) vent, they found evidence for a degassing trend whereby glasses with successively lower CO₂ and H₂O were created as the magma rose through its conduit. The trend could be modeled by closed-system degassing from a magma that started out with 1.2 wt% CO₂ and 5 wt% H₂O in the lower crust. Lower initial CO₂ concentrations would have resulted in significantly different trajectories on a plot of H₂O vs. CO₂.

Following the lead of Newman et al. (1988), other researchers soon began using FTIR spectroscopy to measure the H₂O and CO₂ concentrations in silicate melt inclusions. Anderson et al. (1989) provided the first reliable CO₂ concentrations in silicate melt inclusions from any magma. Studying the 760 ka eruption of the rhyolitic Bishop Tuff, they found evidence for hundreds of ppmw CO₂ dissolved in melt inclusions as well as higher water concentrations than were generally accepted for silicic melts (> 6 wt%). Anderson et al. (1989) calculated saturation pressures above 2 kbar. They concluded that the host quartz crystals were forming in a vapor-saturated melt with vapors containing as much as 45 mol% CO₂. Later work by Wallace et al. (1995) found that dissolved CO₂ concentrations were negatively correlated with incompatible elements such as uranium, and that the slope of the correlation could be explained by the mass fraction of gas present in various parts of the magma chamber. To date, the study of Wallace et al. (1995) is the only one that has used melt inclusions (and CO₂ concentrations) to estimate the amount of gas present in a magma chamber prior to eruption.

Lowenstern (1994) studied volcanic equivalents to the 23 Ma Pine Grove molybdenum porphyry deposit (Utah) and found quartz-hosted melt inclusions with 6–8 wt% H₂O and as much as 960 ppmw CO₂. Calculated saturation pressures ranged as high as 4.3 kbar, requiring that volatile exsolution began at depths of 16 km during ascent to the shallow regions (2–3 km) where the porphyries were emplaced. Other studies showed appreciable CO₂ dissolved in rhyolitic magmas, including the work of Wallace and Gerlach (1994) on the 1991 eruption of Pinatubo (Philippines), and that of Gansecki and Lowenstern (1995) on the ~0.6 Ma Lava Creek Tuff (Yellowstone, Wyoming). Lowenstern et al. (1997) found relatively low CO₂ (40–60 ppmw) and H₂O (2 to 3.5 wt%) concentrations in an A-type rhyolite from the Afar rift of Eritrea. They concluded that the low concentrations were due to shallow entrapment pressures (0.4–0.9 kbar), which was consistent with geologic constraints.

A number of studies of silicic eruptions have found no evidence for CO₂ in phenocryst-hosted melt inclusions. Such eruptions include the 1912 eruption at the Valley of Ten Thousand Smokes (Lowenstern 1993), the climactic 6.8 ka Crater Lake eruption (Bacon et al.

1992), and the 74 ka eruption of the Toba Tuff (Chesner 1998). The absence of detectable CO₂ in the melt inclusions does not mean that CO₂ is absent from the magma, given the ready partitioning of CO₂ into a vapor phase. Lowenstern and Mahood (1991) found no detectable (< 50 ppmw) CO₂ in silicate melt inclusions from peralkaline rhyolites at Pantelleria, Italy. Nevertheless, CO₂ was detected in vapor bubbles found within melt inclusions (Lowenstern et al. 1991). Because the magma chamber was located at shallow depths (2–3 km), little CO₂ was present in the melt phase and nearly all had partitioned into the vapor. Lowenstern et al. (1991) concluded that the CO₂-bearing bubbles were present in inclusions where both melt and a coexisting vapor phase had been trapped simultaneously.

In some systems, CO₂ may be virtually absent due to long-term, open-system degassing of the magma chamber and consequent loss of the least soluble gases. Evidence for such open-system degassing has been inferred by the behavior of sulfur and sulfur isotopes as measured in melt inclusions, matrix glass, and coexisting sulfide minerals (Mandeville et al. 1998). As such, CO₂ could be distilled out of magmas by long-term loss of vapor, combined with little input of new CO₂ from either wallrock or associated magmas.

Evidence for carbonic fluids in granites

Fluid inclusion studies of unaltered granites have provided similar evidence of vapor-saturated silicic magmas in the intermediate to shallow crust. Frost and Touret (1989) studied coeval saline and CO₂-rich fluid inclusions in the Laramie anorthosite complex and concluded that silicate melt, nearly pure CO₂, and hydrosaline melt coexisted at a late magmatic stage of this complex. Calculated isochores allowed them to infer that the inclusions were trapped at 3 kbar and 950 °C. The coexistence of immiscible silicate melt, CO₂-rich vapor, and hydrosaline melt was first shown by Roedder and Coombs (1967) for granitic blocks ejected during eruptions at Ascension Island and has since been studied experimentally by Shinohara et al. (1989; see also Shinohara 1994). Thomas and Spooner (1992) studied CO₂-bearing fluid inclusions in quartz crystals from the Tanco granitic pegmatite and found that the high-temperature “magmatic” inclusions contained dominantly H₂O (~95%) and CO₂, and that this fluid unmixed at low temperatures to form a vapor phase and a dense brine phase. Frezzotti et al. (1994) found evidence that the leucogranites from the Deep Freeze Range of Antarctica were vapor saturated at a pressure of 3 kbar at 750 °C with a fluid having $a_{\text{H}_2\text{O}} = 0.5$, with the remainder consisting mostly of CO₂. Nabelek and Ternes (1997) interpreted CO₂-rich fluid inclusions from the Harney Peak Granite (Black Hills, South Dakota) to be primary magmatic vapors trapped at 3.5 kbar in equilibrium with a granitic melt containing 3.5 wt% dissolved H₂O and 1,500 ppmw dissolved CO₂.

Crustal sources of carbon

Granites and silicic volcanic rocks are more likely to have an origin through crustal melting than their mafic counterparts, and CO₂ concentrations in rhyolites and dacites may be augmented by partial melting and assimilation of crustal materials. The formation of skarns often includes breakdown of carbonate-bearing rocks by infiltration of water-rich magmatic fluids (Einaudi et al. 1981; Meinert et al. 1997). Such a process is certain to add CO₂ to the magma, while creating decarbonated calc-silicate assemblages and carbonate-rich melts (Lentz 1999). Graywackes, calcareous sandstones, and many hydrothermally altered rocks may contain sufficient carbon to provide a source of CO₂ to crustal melts and ascending mafic magmas. One difficulty in identifying this source of carbon in silicic magmas is the lack of igneous phenocrysts that incorporate carbon. With the exception of a small carbonate component in fluorapatite, CO₂ is partitioned almost entirely into outgassed fluids and has a very low abundance in analyses of volcanic rocks and igneous intrusions (White et al. 1999). Where present, such carbon may be sub-solidus in nature (White et al. 1999). As a result, only direct sampling of magmatic gases is likely to provide insight into the source of CO₂ in magmas. Unfortunately, at this point, most isotopic data for carbon in volcanic gas is from mafic systems.

Can vapor-saturated magmas ascend through the crust and erupt?

Magma ascent

As discussed above, many recent studies provide evidence for CO₂-rich vapors in magmas within the middle to upper crust. It is a commonly held belief that vapor-saturated magmas cannot ascend through the crust without freezing, and that addition of CO₂ to a magma should also cause it to crystallize. However, the presence of vapor is not always likely to impede the movement of magmas through the crust.

Tuttle and Bowen (1958) stated that H₂O-saturated anatectic magmas that reside at the haplogranite ternary minimum cannot rise through the crust because any loss of H₂O via degassing would move the solidus to higher temperatures, resulting in crystallization and solidification. This statement has been corroborated by numerous subsequent studies, but it overlooks the probability that most anatectic melts are created at depths where water saturation would require > 10 wt% dissolved H₂O. If magmas instead contain less dissolved water, as has typically been inferred in many of the studies listed above, they should be able to ascend through the crust without impediment, even if they become saturated with a multicomponent vapor containing other gases in addition to H₂O.

Because CO₂ dissolves in its molecular form in silicic melts at crustal pressures (Blank et al. 1993), it has little

effect on melt structure and controls phase equilibria primarily through dilution of coexisting vapors and consequent reduction of H_2O activity. Holloway (1976) showed that closed-system equilibration of silicic magma with CO_2 -bearing vapor can buffer the H_2O concentration of the melt, causing P_{H_2O} to stay constant, or increase, during magma ascent. This process is illustrated in Fig. 5 (diagram similar to those in Anderson et al. 1989 and Lowenstern 1994). The trends for decompression degassing show that ascent will have minimal effect on dissolved H_2O concentration and, therefore, on melt structure and phase relations. In other words, if degassing does not cause the dissolved H_2O content to change appreciably, then there will be no impetus towards crystallization. In fact, slow adiabatic (isenthalpic) ascent of the magma alone will be likely to cause a small temperature increase (Waldbaum 1971). Thus, during decompression, the vapor-saturated magma will not necessarily crystallize and can rise into the upper crust (4–6 km depth). Once the magma rises to shallow regions, the 1–4 km depths associated with epithermal and porphyry ore deposits, subsequent ascent will likely force degassing of H_2O -rich (but still CO_2 -bearing) fluids. This process will inevitably begin to affect the solidus and to induce crystallization.

Magma eruption

Often, magma does not erupt but instead ponds in the crust to crystallize as intrusions. The creation of a lode gold deposit from a magmatic source requires that at least some magma remains behind in the crust and undergoes devolatilization to release the metal-bearing

fluids. Just as the presence of a vapor phase does not necessarily hasten magma crystallization, it also does not imply immediate eruption. Shinohara et al. (1995) presented a model whereby bubble-rich magmas undergo open-system degassing at shallow depths (2–3 km) to create Climax-type molybdenum porphyry deposits. In such a scenario, the magma is sufficiently volatile-rich that it can outgas as a porous open system without further bubble growth and expansion, allowing magma that loses its bubbles to sink relative to the volatile- and molybdenum-bearing magma rising from depth. This convective model would work best for volatile-rich magmas; they would be less eruptible because they can become permeable (see Eichelberger et al. 1986) and lose exsolved gas at greater depths than less gas-rich magmas.

As discussed above, thermodynamics and phase diagrams predict that rising hydrous magmas should crystallize before reaching the surface if ascent took place under equilibrium conditions. If the vapor-saturated magma represented in Fig. 5 were to rise to depths where pressures are less than 2 kbar, then the vapor phase would become increasingly H_2O -rich as water is drawn out of the melt. At low pressures, degassing has a pronounced effect on dissolved H_2O concentration and should inhibit magma ascent by inducing crystallization. Even so, we know from modern volcanologic studies that vapor- (and H_2O -) saturated magmas can and *do* rise and erupt from relatively shallow magma chambers (< 11 km depths; e.g., Pinatubo, Bishop Tuff, Cerro Negro, and all the other volcanic events summarized above). The rhyolitic melts that form glassy lavas, such as obsidian domes, although clearly H_2O -saturated during much of their final ascent to the surface (Eichelberger et al. 1986; Newman et al. 1988; Taylor 1988), are able to rise and erupt without significant crystallization and can flow for kilometers over the Earth's surface as supercooled liquids. Their ability to do so is a result of the sluggish crystallization kinetics of silicic melts and the decrease in viscosity caused by the presence of bubbles in magmas (Bagdassarov and Dingwell 1992).

The most likely situation where the presence of CO_2 would impede magma ascent would be where a CO_2 -poor magma was created in the mantle or deep crust at a relatively low temperature. As it rose through the crust, if there were a mechanism to add large amounts of CO_2 to the magma (e.g., by assimilation/melting of carbonaceous sediments or limestone; Lentz 1999), the resulting CO_2 -rich vapor phase would draw water out of the melt, potentially causing the magma to cross its solidus and crystallize (Fig. 6).

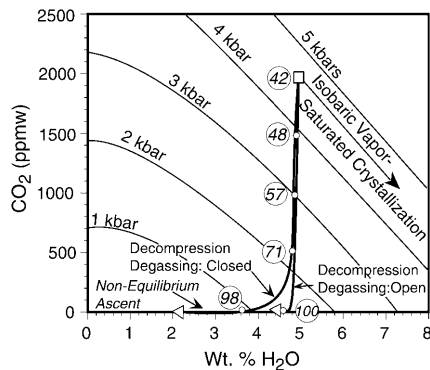


Fig. 5 Solubility plot for the system rhyolite– H_2O – CO_2 at 750 °C. Lines labeled with units of pressure represent isobars that display solubility of H_2O and CO_2 as function of fluid composition (see Fig. 3). Isopleths not shown (see Fig. 3). Trend parallel to isobars shows effect of crystallization on vapor-saturated melt at ~4.6 kbar starting with 2,000 ppmw CO_2 and 5.0 wt% H_2O . Decompression-induced degassing trends show paths of isothermal ascent, in equilibrium with the vapor (closed system) or allowing created vapor to escape (open). Numbers along paths list mol% H_2O in vapor (remainder being CO_2). The decompressing magma should degas without significant crystallization until it reaches virtual H_2O -saturation (X-axis). At that point, magma ascends as a supercooled liquid, as in all silicic eruptions

The degassing process

Given the evidence for CO_2 -bearing vapors in a wide range of crustal magmas, it becomes important to understand the general chemical behavior and characteristics of such vapors. One generality is that early-exsolved vapors will always be more CO_2 -rich than those

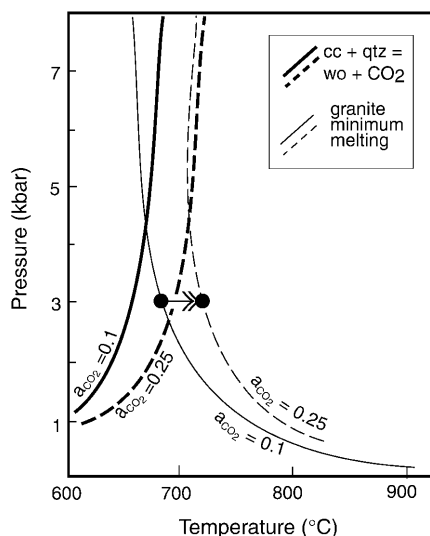


Fig. 6 Pressure versus temperature diagram for the granite solidus (*thin lines*) and the decarbonation of calcite (*thick lines*; figure after Holloway 1976). A vapor-saturated magma near its solidus and with a_{CO_2} in the vapor equal to 0.1 would be supercooled (relative to its solidus) by about 35 °C if the magma were flooded with enough CO_2 to move the vapor-phase activity of CO_2 to 0.25 (*arrow*). This would be possible, for example, by heating siliceous limestones above 600 °C, causing calcite (*cc*) + quartz (*qtz*) to form wollastonite (*wo*). This reaction would eventually slow down due to the production of CO_2

exsolved later. As the magma rises and/or cools, the low solubility of CO_2 relative to H_2O will cause it to partition preferentially into any exsolving vapor phase. The earliest-formed vapors may also be (relatively) rich in other magma-insoluble gases such as the noble gases and N_2 (Giggenbach 1997). Both closed- and open-system degassing of any natural silicate melt will result in progressively more H_2O -rich vapors with time. This will be the case whether degassing is caused by depressurization or crystallization (“second boiling”). If bubble formation is delayed until the magma reaches shallow depths, partitioning into the vapor may be dominated by H_2O , swamping any CO_2 in the system. Magmas can also contain little CO_2 if their differentiation is protracted and magma-insoluble gases are distilled away over time. Evidence for open-system degassing has been noted by Mandeville et al. (1998) and is discussed above in the section on silicic magmas.

CO_2 is not the only carbon-bearing species that will be present in magmatic emanations. Concentrations of as much as ~0.4 wt% CO occur in some hot, low f_{O_2} basaltic gases (Table 3 of Symonds et al. 1994), about 5% of the abundance of CO_2 . More typically, CO is two to four orders of magnitude less abundant than CO_2 , particularly in andesitic and dacitic gases and those with $f_{\text{O}_2} > \text{QFM}$. Methane (CH_4) is extremely rare in volcanic gas and is usually attributed to contamination with geothermal and low-temperature crustal gases (Symonds et al. 1994) or initial oxidation states well below QFM. However, as magmatic fluids re-equilibrate at lower temperatures, methane concentrations will increase, and

CH_4/CO_2 ratios may be appreciable at the temperatures expected for hydrothermal mineralization in intrusion-hosted gold deposits (300–450 °C).

Another important concept to consider is the effect of CO_2 on unmixing of the volatile phase, particularly in silicic magmas where temperatures may not exceed 800 °C. Under such conditions, halides and some sulfates have extremely low solubility in CO_2 -bearing vapors. For example, in the H_2O – NaCl system at 700 °C, fluids with more than 5 wt% NaCl will unmix to form immiscible vapor and brine phases at any pressure lower than about 1.1 kbar (Sourirajan and Kennedy 1962). However, addition of 20 wt% or more CO_2 will cause such a fluid to unmix at any pressure lower than about 5 kbar (Bodnar and Sterner 1987; Joyce and Holloway 1993). Increasing temperature will only increase the likelihood of unmixing (as long as the temperature is below the melting point of halite; 800 °C at 1 bar). This means that the conditions where silicic magmas are saturated with both a vapor and brine (hydrosaline melt) will be common in the middle to upper crust. Given the different partitioning behavior of metals between melt, vapor, and brine (Candela and Piccoli 1995), the presence of CO_2 will increase the likelihood of fractionation of metals among fluids with different densities and transport properties.

CO_2 in hydrothermal fluids and surface manifestations

Although this review focuses primarily on CO_2 in magmas, it is appropriate to discuss some general concepts that describe the evolution and behavior of carbonic fluid in hydrothermal systems. As magmatic vapors, brines, and supercritical fluids leave the magma and enter hydrothermal systems, they can potentially act as mineralizing fluids. Just as in the magma, the presence of CO_2 will promote immiscibility and creation of a vapor phase that will incorporate sulfur gases and noble gases as well as CO_2 and steam.

Pressure decreases will tend to cause boiling or effervescence of CO_2 - and H_2S -bearing vapors. Such boiling events may be most dramatic in the high-temperature (300–450 °C) environments envisioned for intrusion-hosted Au deposits. At high temperatures, rock loses strength and becomes ductile, which spurs annealing and reduction of rock permeability. Pressure can build until rapid fluid-release events force brittle fracturing, sometimes causing pressure to decline from lithostatic to hydrostatic gradients (Fournier 1999). Such catastrophic depressurization will force boiling of hydrothermal solutions and release of CO_2 -rich vapors. Sheeted hydrothermal veins may result from repetition of these pressure fluctuations with their associated boiling, mineral precipitation reactions, and subsequent annealing.

At temperatures above 300 °C, CO_2 strongly partitions into the vapor phase and has a relatively low solubility in aqueous fluids (Rimstidt 1997). The vapor can be relatively unreactive because carbonic acid weakly

dissociates at temperatures above 300 °C (Bischoff and Rosenbauer 1996; Giggenbach 1997). As temperatures fall, however, carbonic acid (H_2CO_3) more readily dissociates, allowing it to react with rock to leach cations and form bicarbonate-rich geothermal fluids (Bischoff and Rosenbauer 1996). Even at low temperatures, CO_2 has only limited solubility in geothermal waters. For example, at 200 °C, a 1 mol% solution of CO_2 in pure H_2O has a partial pressure of 66 bar (data from Chapter 4 of Henley et al. 1984), whereas that for water is 16 bar. Thus, at or below 82 bar, a CO_2 -dominated vapor will exsolve from this solution as bubbles. Addition of other gases or the presence of NaCl in solution will increase the vapor pressure and thus the pressure at which bubbles will form. At the Broadlands geothermal area, New Zealand, evidence for CO_2 -saturated geothermal fluids extends to depths of 2,500 m (p. 54, Henley et al. 1984). As a result, CO_2 gas often accumulates in the shallow crust and can result in hydrothermal and geothermal well-field explosions (e.g., Hedenquist and Henley 1985).

Volcanic regions have long been known as subject to CO_2 buildup. The 1986 disaster at Lake Nyos, Cameroon, evidently occurred due to deep volcanic degassing and resultant accumulation of CO_2 -saturated water in the deep lake, followed by catastrophic overturn and release of a large, CO_2 gas cloud, killing over 1,700 people (Kusakabe 1996). At Mammoth Mountain, California, ongoing diffuse degassing of 530 t/day CO_2 has caused about 30 ha of forest to die and is a continuing source of concern (Farrar et al. 1995, 1999). The gas appears to emanate from a vapor-rich gas reservoir located in seismically active zones within 3 km of the surface (Julian et al. 1998). The isotopic composition of the gas is consistent with derivation from magma and the tree-kill began after a 1989 seismic swarm that was apparently related to intrusion of a basaltic dike (Farrar et al. 1995). On Mt. Etna, Italy, residents have long been aware of diffuse percolation of CO_2 through the volcanic edifice, resulting in CO_2 -charged groundwater and diffuse degassing that constitutes a significant percentage of the total CO_2 released by the volcano (Allard et al. 1997).

Clearly, CO_2 behaves as a highly volatile species, both within magmas and in superjacent hydrothermal systems. In magmas, there are no crystalline components that incorporate CO_2 or carbonate groups (except for a very minor amount in apatite) and CO_2 solubility is generally low in the melt. In hydrothermal systems, CO_2 is not highly soluble under most conditions and precipitates as carbonate minerals primarily at lower temperatures. As a result, CO_2 can exsolve from hydrothermal waters and groundwaters to escape to the surface.

Metal partitioning into CO_2 -bearing fluids

Given the evidence for CO_2 -bearing fluids in magmatic systems and, in particular, associated with gold-bearing intrusions (Newberry et al. 1995; Thompson et al. 1999 and references therein), one must ascertain the impor-

tance of carbonic fluids in transporting ore-forming metals. Perusing a recent compilation on melt/vapor/brine partition coefficients (Candela and Piccoli 1995), it becomes apparent that little is known about the role of CO_2 as a ligand, and little firm evidence exists that CO_2 plays a direct role in ore formation. Seward and Barnes (1997) demonstrate that based on Lewis acid-base behavior of metals and ligands, one would not predict metal-carbonate complexes to be particularly stable. Where experimental studies have explored the partitioning of metals into CO_2 -rich fluids, most have concluded that increasing concentrations of CO_2 tend to decrease metal vapor/melt partition coefficients (e.g., Webster et al. 1989).

A few studies, however, have documented apparent mobilization of metals by CO_2 -rich fluids, primarily in the deep crust. Wendlandt and Harrison (1979) demonstrated the ability of carbonate-rich melts to transport LREE and discussed the importance of LREE enrichments in fenites and metasomatized mantle. Keppler and Wyllie (1990) found limited, but significant, uranium mobility in high-temperature magmatic fluids at moderate crustal pressures (2 kbar). They noted that increasing CO_2 concentrations in the fluid were accompanied by higher uranium concentrations. In a petrographic study of tungsten-mineralized rocks, Higgins (1980) noted a correlation between CO_2 -rich fluid inclusions and tungsten concentrations. However, experimental studies have yet to document this relationship.

We are, therefore, left with a preponderance of studies that show evidence for CO_2 -bearing, fluid inclusions in gold-bearing intrusions and the apparent lack of experimental evidence that CO_2 acts as a ligand for most ore-associated metals. One potential explanation for the apparent discrepancy would be simply that CO_2 is a very common gas in igneous and hydrothermal systems and should be ubiquitous regardless of whether it has a role in the ore-forming process. Appreciable $\text{CO}_2/\text{H}_2\text{O}$ ratios (e.g., >0.1) could indicate that the magma did not undergo a protracted period of differentiation and degassing, which would have caused loss of the more magma-insoluble components such as CO_2 . Deep degassing, and input of volatiles from underlying magmas could also result in the presence of appreciable CO_2 in fluids derived from the ore-hosting magma. It is also likely that CO_2 acts as a fugitive agent in the hydrothermal fluid, readily causing unmixing of the fluid to create a separate vapor phase. Heinrich (1995) summarizes evidence for vapor-phase transport of copper in a number of intrusion-hosted deposits, and especially in tin deposits. Audetat et al. (1998) give an even more striking example of vapor-phase transport of copper and boron, presumably by sulfide complexes. They stress that gold should also be complexed by sulfide in the vapor phase. If this is the case, the presence of CO_2 will hasten the creation of a vapor phase causing H_2S , and possibly HCl, to move into the vapor and act as ligands for some metals. At the same time, effervescence of CO_2

from the fluid will result in a decrease in P_{CO_2} and an increase of pH in the remaining liquid, causing important mineral precipitation reactions (e.g., Simmons and Christenson 1994) and destabilization of ligands such as gold bisulfide (Seward 1973). Therefore, although the effect of CO_2 on mineralization may not be direct, this common gas plays a key role in the creation and evolution of metal-bearing vapors in ore-forming systems.

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