Direct dating of Fe oxide-(Cu-Au) mineralization by U/Pb zircon geochronology

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ABSTRACT
We present results for direct dating of Fe oxide-(Cu-Au) (iron oxide, copper, gold—IOCG) mineralization by U/Pb zircon geochronology. Constraining the timing of mineralization has important geodynamic implications for the processes involved in the genesis of these types of deposits and the tectonic evolution of rocks associated with these deposits. Hydrothermal zircon crystals were separated from four IOCG-type ore deposits associated with the Lyon Mountain Granite in the Adirondack Mountains, United States. Zircon grains from these low-Ti magnetite deposits reveal at least two periods of mineralization; one episode ca. 1039 Ma and a second between ca. 1015 and 1000 Ma. Previous age determinations of these deposits were constrained by the age of the altered host granitoids, and the assumption that Fe mineralization was directly related to pluton emplacement. Zircon crystals extracted from the ore yield ages that show that ore mineralization was episodic and younger than pluton emplacement.

INTRODUCTION
Iron oxide-(Cu-Au) (iron oxide, copper, gold—IOCG) deposits are a class of ore deposits whose defining characteristics vary significantly (e.g., Hitzman et al., 1992). Some deposits contain significant amounts of Cu, Au, and U, such as those at Olympic Dam, Australia (e.g., Reynolds, 2000), whereas the dominant ore at Kiruna, Sweden, is magnetite and apatite (Harlov et al., 2002). The unifying characteristics of all these deposits are high concentrations of low-Ti Fe oxide minerals (magnetite and hematite), pervasive hydrothermal alteration (Na, K, Si, seritization), and an extensional tectonic setting (Hitzman et al., 1992).

Several studies have attempted to constrain the timing of IOCG-type mineralization by dating zircon in the altered host rocks associated with these deposits (e.g., Mortimer et al., 1988). Other studies have dated minerals in the ore such as apatite and titanite (e.g., Romer et al., 1994; Gelich et al., 2005), or monazite (e.g., Grainger et al., 2008), or Re-Os dating of molybdenite (e.g., Mathur et al., 2002). Dating the host rock, however, assumes that the growth of zircon is coeval with Fe mineralization. Accessory minerals that are directly linked with ore mineralization provide a less ambiguous means of dating IOCG mineralization. Iron oxide mineralization is often accompanied by the growth of apatite and titanite (Hitzman et al., 1992); however, those minerals may incorporate common Pb (i.e., 206Pb) in their structure, and if their 206Pb/204Pb ratios are low, this will preclude obtaining precise ages. In this study we directly dated Fe mineralization by identifying hydrothermal zircon from four IOCG-type ore deposits in the Lyon Mountain Granite from the Adirondack Highlands in New York State. Zircon is a more robust geochronometer and as such should provide more reliable age constraints on the timing of mineralization.

GEOLOGICAL SETTING
The Adirondack Highlands (Fig. 1) are dominated by a ca. 1150 anorthosite-mangerite-charnockite-granite suite that was metamorphosed during the Ottawan orogeny between 1090 and 1040 Ma and is intruded by syntectonic to late tectonic granites (McLelland et al., 2001). The Lyon Mountain Granite crops out extensively in the northeastern Adirondack Highlands and is the host to numerous low-titanium magnetite IOCG-type deposits (e.g., Whitney and Olmsted, 1988). The Lyon Mountain Granite underwent extreme metasomatism by potassic-and sodic-rich fluids, accompanied by enrichment in F and P, and mobilization of high field strength elements, including Zr, Y, U, and light and middle rare earth elements (REEs) during Fe mineralization (Foose and McLelland, 1995; Whitney and Olmsted, 1993; McLelland et al., 2002). The Lyon Mountain Granite consists of mesoperthite granite and, where altered, microcline granite and/or albite granite. All lithologies contain disseminated magnetite as the predominant mafic mineral. A gneissic fabric may be present but varies from pronounced to nonexistent.

LOW-TITANIUM MAGNETITE DEPOSITS
The ores are composed of magnetite and/or hematite, and typically include apatite, quartz, feldspar, clinopyroxene, and minor zircon. Fluid temperatures of 565–675 °C were estimated from quartz-magnetite δ18O fractionation (McLelland et al., 2002). The Lyon Mountain Granite orebodies are associated with shear zones and fold hinges, and with the contacts of the Lyon Mountain Granite with other units (Postel, 1952; Whitney and Olmsted, 1993). The orebodies are generally conformable with the gneissic fabric, but locally crosscut the fabric at a high angle. Barren zones as wide as 150 m that are nearly devoid of magnetite occur in the granite immediately adjacent to the orebodies (Hagner and Collins, 1967). The locations of samples used in this study are shown in Figure 1. Detailed descriptions of the individual ore deposits in this study are given in the GSA Data Repository (Item DR1*).

Numerous workers have discussed the origin of low-Ti magnetite ores in the Lyon Mountain Granite; these origins include (1) immiscible magmatic Fe-rich fluids (e.g., Postel, 1952); (2) the breakdown of preexisting mafic silicates (Hagner and Collins, 1967); (3) eruption of Fe oxide magmas (Whitney and Olmsted, 1993); and (4) surface-derived saline fluids that have interacted with the latest stages of pluton emplacement (McLelland et al., 2002). Previously, the timing of Fe mineralization in the Lyon Mountain Granite was constrained through inference by its close association with the Lyon Mountain Granite host rocks (Foose and McLelland, 1995; Selleck et al., 2004).

*GSA Data Repository item 2009060, Item DR1, ore deposit descriptions; Item DR2, analytical techniques; Table DR1, ion microprobe U-Th-Pb results; and Figure DR1, complementary cathodoluminescence and backscattered electron images of representative zircon samples, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
U-Pb SECONDARY ION MASS SPECTROMETRY GEOCHRONOLOGY

Uranium-Th-Pb zircon analyses for the four ore and two granite host samples were done using the Cameca ion mass spectrometer 1270 ion microprobe at the Swedish Museum of Natural History following the methods described by Whitehouse et al. (1999) and modified in Whitehouse and Kamber (2004). Concordia ages for samples that yield overlapping concordant points were calculated using Isoplot (Ludwig, 2003). The mean square of weighted deviates (MSWD) indicates whether uncertainties in the Concordia age can be explained entirely by assigned analytical error on individual data points (MSWD ~1 or lower). Details of the analytical techniques are given in Item DR2. The U/Pb data are presented in Figure 3 and Table DR1. All age uncertainties in the paper and associated figures are 2σ. Errors in Table DR1 are 1σ.

Magmatic zircon crystals from the host granite typically are brown to pink, elongate, well faceted, and highly fractured (Fig. 2A), and may contain inclusions of apatite or quartz. These grains are often zoned with respect to U and Hf and some contain older inherited cores (Fig. 2A).

Zircon is typically found as inclusions in quartz or feldspar or at grain boundaries.

Hydrothermal zircon grains from the magmatic ore are typically blocky, clear, and featureless in backscattered electron (BSE) images (Fig. 2B). Some contain irregular patchy zoning in BSE or cathodoluminescence (CL) imaging (Fig. DR1). Some of the ore zircon crystals analyzed contain interior regions with different U and Hf contents that produce variations in the BSE signal and appear to be cores (Fig. DR1); however, these inner zones yield ages within error of the outer regions in the crystals (Table DR1). Zircon grains are generally free of melt or fluid inclusions, but may contain small apatite, Fe oxide, or quartz inclusions. Zircon crystals occur in association with magnetite, apatite, fluorite, calcite, quartz, and chlorite.

Zircon grains from the granite <1 m above the contact with the orebody at Palmer Hill yield a concordant age of 1062.6 ± 5.5 Ma (2σ) (Fig. 3A). Samples from the ore yield an age of 1038.9 ± 4.4 Ma (2σ) (Fig. 3B). Zircon from the granite adjacent to the orebody at Arnold Hill yielded an age of 1060.7 ± 4.5 Ma (2σ) (Fig. 3C). The age for zircon crystals from the Arnold Hill ore is 1016.1 ± 7.1 Ma (2σ) (Fig. 3D). The Skiff Mountain ore is dated as 1000.9 ± 9.2 Ma (2σ) (Fig. 3E). The Old Bed orebody contains zircon crystals that are very large (up to 10 mm). They are typically dark brown and highly metamict. Because of the extreme metamictization, variable degrees of Pb loss have affected this sample. Two approaches were therefore used to calculate a minimum 207Pb/206Pb age. A statistically valid age was calculated using a weighted mean average. Analyses were added (n = 28) until the MSWD was >1. This approach produced an average 207Pb/206Pb age of 1060.7 ± 4.5 Ma (2σ) (Fig. 3F). However, this is a weighted average of samples that have undergone significant Pb loss. Analytical error alone cannot explain the difference between the oldest measured ages and the age calculated by this weighted average. If we assume that the oldest ages represent the least amount of Pb loss, then the oldest analyses are a minimum age. A weighted average of the four oldest samples (n = 4) yields a 207Pb/206Pb age of 1020.0 ± 11 Ma (2σ) (Fig. 3F).
DISCUSSION

Uranium-Pb zircon ages calculated from low-Ti magnetite deposits in the Lyon Mountain Granite are 20–60 m.y. younger than their host granites. These age data are supported by the earlier work of McLelland et al. (2001), who used the sensitive high-resolution ion microprobe to date the Lyon Mountain Granite from several nearby localities as between 1059 and 1047 Ma. It seems unlikely, therefore, that the iron mineralization is directly related to emplacement of the granites that host the ore deposits. Three possibilities for the formation of zircon in these iron oxide deposits are: (1) postemplacement metamorphic fluids; (2) Fe oxide–rich magmas intruding as dikes and sills; and (3) the zircons in the ores are hydrothermal in origin, with mineralizing fluids coming from deep circulating meteoric waters and/or brines, or younger and as yet unidentified magmatism.

Metamorphic fluids seem the least likely hypothesis. Small leucogranite bodies that were emplaced during regional extension and numerous dikes that crosscut the gneissic fabric of the Lyon Mountain Granite have been dated between 1045 Ma and 1030 Ma in the Adirondacks (McLelland et al., 2001; Selleck et al., 2005). Because U/Pb ages from the ore deposits have contemporaneous or younger ages than these dikes, the orebodies could not have been significantly metamorphosed or deformed.

There is some evidence that these deposits could be Fe-rich magmas (e.g., nelsonites) that intruded the Lyon Mountain Granite as dikes and sills. The contacts of some deposits are very sharp with the surrounding granite or ores, and may be pegmatitic in nature. Iron oxide magmas have been proposed sources for other IOCG deposits (e.g., Naslund et al., 2002). The similarity of magnetite, apatite, and quartz ores with nelsonite magmas is compelling; however, nelsonite magmas are enriched in Ti (as well as Fe and P), and all of these orebodies contain low-Ti oxides. Also, nelsonite magmas are typically associated with anorthosite-gabbro intrusions. Though very large anorthosite bodies are common in the Adirondack highlands, these intrusions are ~100–150 m.y. too old to be responsible for ore formation in the Lyon Mountain Granite (McLelland et al., 2001).

Several papers have been written on the hydrothermal origin of IOCG deposits (e.g., Hitzman et al., 1992; Barton and Johnson, 1996, and references therein). The presence of vein fluorite and fluorite intergrown with magnetite andapatite at the Palmer Hill mine suggests that the ore is hydrothermal. At Arnold Hill the presence of calcite, microcrystalline quartz, and chlorite in brecciated zones associated with Fe mineralization also suggests a hydrothermal origin. Extensive Na and K alteration of perthitic feldspar in the host granites requires a hydrothermal fluid or late magmatic and/or hydrothermal fluid. The scavenging of disseminated magnetite from the host rock and production of magnetite from the breakdown of clinozoisite is also consistent with an ore that is hydrothermal in nature and may be the source of Fe for the orebody (Hagner and Collins, 1967).

The presence of hydrothermal zircon in an ore requires that Zr was highly mobile during mineralization. Zirconium is generally thought to be an immobile element during rock alteration; however, the presence of F-rich fluids and alkaline fluids, Zr may become available, and mobile, from the breakdown of aegirine and arfedsonite in the host rocks (Rubin et al., 1993). The presence of F-bearing minerals indicates that F was present during mineralization. Other possible reservoirs of Zr include ilmenite, titanite, rutile, and garnet (Bea et al., 2006). In some cases it may be possible to use Th/U ratios to distinguish hydrothermal from magmatic zircon grains. However, some hydrothermal zircon show depletion in Th (Rubin et al., 1993), while others may show an increase in Th (Hoskin, 2005). Thorium/U ratios in the Arnold Hill ore zircon are virtually indistinguishable from those of the host granite, whereas at Palmer Hill there is a distinct difference in Th/U ratios of the ore and granite zircon (Table DR1). These differences alone do not preclude that ore-related zircon at Palmer Hill or Arnold Hill are hydrothermal in origin. Zircon grains in the ore could not be an immobile element during rock alteration; however, the presence of F-bearing minerals indicates that F was present during mineralization. Other possible reservoirs of Zr include ilmenite, titanite, rutile, and garnet (Bea et al., 2006). In some cases it may be possible to use Th/U ratios to distinguish hydrothermal from magmatic zircon grains. However, some hydrothermal zircon show depletion in Th (Rubin et al., 1993), while others may show an increase in Th (Hoskin, 2005). Thorium/U ratios in the Arnold Hill ore zircon are virtually indistinguishable from those of the host granite, whereas at Palmer Hill there is a distinct difference in Th/U ratios of the ore and granite zircon (Table DR1). These differences alone do not preclude that ore-related zircon at Palmer Hill or Arnold Hill are hydrothermal in origin. Zircon grains in the ore could...
not have been inherited from the host Lyon Mountain Granite, however, because of the discrepancy in ages between the host rocks and the ore and the textural relationship of ore zircon to possible hydrothermal minerals such as apatite, fluorite, and altered feldspars.

The most plausible explanation for the origin of the Fe mineralization is penetration of hydrothermal fluids along faults related to extension and orogenic collapse. These fluids may be presumably rich in alkalis, F, F, REEs, Y, U, and Zr. Initial Fe mineralization ca. 1039 Ma at the Palmer Hill mine is coeval with syenotextured leucogranite bodies and dikes. Fluids and heat required for the formation of the oldest ore deposits may have been supplied by these intrusions. However, the older granites that host the ore deposits are too old to have supplied the heat and fluids needed for mineralization. It is not clear if subsequent Fe mineralization ca. 1020 Ma and ca. 1000 Ma was the result of as yet undiscovered plutonism and/or episodic extension and secondary fluid penetration. If these younger ages were the result of Pb loss, we would expect to see a continuum of ages with each sample.

CONCLUSIONS

The first direct dating of low-Ti magnetite ore by U/Pb zircon geochronology indicates that Fe mineralization was protracted and episodic and could not be related to emplacement of the host granites. These data are consistent with Fe mineralization being the result of hydrothermal fluid alteration during a period of extensional tectonics. Direct U/Pb dating of zircon crystals from the ore provides a more robust method for dating IOCG deposits than other minerals that may be susceptible to the effects of common Pb or that provide only indirect dates from the host rocks. Understanding the timing of Fe mineralization and hydrothermal alteration provides important information for ore petrogenesis, crustal fluids, and the tectonic evolution of the regions that host these deposits.

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