Chemical Geology 385 (2014) 70–83

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Gold concentrations in metamorphic fluids: A LA-ICPMS study of fluid inclusions from the Alpine orogenic belt

K. Rauchenstein-Martinek [a], T. Wagner [b,*], M. Wälle [a], C.A. Heinrich [a]

[a] ETH Zurich, Department of Earth Sciences, Institute of Geochemistry and Petrology, Clausiusstrasse 25, 8092 Zurich, Switzerland

[b] Department of Geosciences and Geography, Division of Geology, University of Helsinki, Gustaf Hällströmin katu 2a, FI-00014 Helsinki, Finland

ARTICLE INFO

Article history:
Received 22 January 2014
Received in revised form 18 July 2014
Accepted 20 July 2014
Available online 30 July 2014

Editor: David R. Hilton

Keywords:
Gold deposit
Fluid inclusions
LA-ICPMS
Thermodynamic modeling
Metamorphic fluids
Alps

ABSTRACT

Vein and shear-zone hosted gold deposits in orogenic terrains of Archean to Phanerozoic age are formed from dominantly metamorphic fluids. It is debated, however, whether normal crustal source rocks are adequate to generate economic deposits, or whether selectively gold-enriched sources such as mafic to ultramafic lavas, black shales or an input of magmatic fluid make a decisive difference between the formation of high-grade deposits and barren vein systems. As an essential baseline study in this debate, we have analyzed the metal and sulfur content of fluid inclusions in barren veins across a prograde sequence from greenschist to amphibolite facies in the Central Alpine metamorphic belt. Comparison of the analyzed fluid compositions with thermodynamic solubility calculations shows that the fluids record metamorphic dehydration, decarbonation and desulfidation of the continental crust. However, gold with concentrations of 0.003 to 0.03 ppm is increasingly undersaturated in the highest-temperature aqueous–carbonic fluids, which otherwise resemble those forming major gold deposits elsewhere. Our results show that the regional-metamorphic fluids could carry 10–1000 times higher gold concentrations, implying that pre-enriched source rocks or hydrous magmas may play an essential role in generating highly gold-endowed orogenic belts.

1. Introduction

Metamorphic fluids are formed by extraction of small amounts of volatiles (<2 to 6% by weight) from large crustal terrains (Yardley, 1983; Cox et al., 1987; Ague, 2003; Tomkins, 2010; Vry et al., 2010). It is widely accepted that the major element and isotopic composition of metamorphic fluids are inherently rock-buffered, i.e., controlled by equilibria with the minerals of their source rocks (Ridley and Diamond, 2000; Oliver and Bons, 2001; Phillips and Evans, 2004; Phillips and Powell, 2009, 2010). Metamorphic fluids are mostly composed of H_2O, CO_2 and NaCl, and common minor components are CH_4, H_2S, N_2, KCl, $CaCl_2$ and H_3BO_3, as shown by a large number of fluid inclusion studies from orogenic belts worldwide (e.g., Yardley et al., 1993; Mullis et al., 1994). Reflecting the host rock-buffering control and metamorphic pressure–temperature conditions, the bulk composition of metamorphic fluids changes in a systematic way with increasing temperature–pressure conditions along regional-metamorphic gradients. Regional zoning of fluid inclusion compositions is well documented for the Central Alps (Poty et al., 1974; Frey et al., 1980; Mullis et al., 1994; Frey and Ferreiro Mählmann, 1999; Mullis et al., 2002; Tarantola et al., 2007, 2009). Fluid inclusions from successive metamorphic zones, ranging from sub-greenschist to amphibolite facies, predominantly contain liquid hydrocarbons, CH_4, H_2O and CO_2, respectively, consistent with the metamorphic petrology of devolatilization reactions (Ague, 2003).

While the bulk composition of metamorphic fluids regarding major volatile components is well documented, there is only limited knowledge about the concentrations of minor components and ore metals such as Cu, Zn, Pb, Ag and Au in metamorphic fluids. A recent LA-ICPMS study of individual fluid inclusions from the Alpine orogenic belt has reported concentration data for Cu, Zn and Pb on the order of few ppm (Miron et al., 2013), while a similar study of fluid inclusions from a Variscan slate belt could not detect these ore metals (Marsala et al., 2013). More comprehensive data that document compositional variations along a prograde metamorphic facies series provide an essential baseline for understanding the role of metamorphic fluids in the formation of major ore deposits. Such baseline data is particularly relevant for interpreting the origin of orogenic gold deposits, which occur in metamorphic terrains and are thought to involve ore fluids produced by metamorphic devolatilization (Groves et al., 1988; Goldfarb et al., 2001; Groves et al., 2003; Jia et al., 2003; Goldfarb et al., 2005; Phillips and Powell, 2009, 2010; Hronsky et al., 2012). A fundamental issue is to assess whether ore metal concentrations in metamorphic fluids are limited by mineral solubility (Yardley, 2005) or whether they are controlled by metal and sulfur availability in the devolatilizing source region (Tomkins, 2010). For gold, pyrite is the principal mineralogical source and metamorphic reactions that control pyrite breakdown

* Corresponding author.
E-mail address: thomas.wagner@helsinki.fi (T. Wagner).

http://dx.doi.org/10.1016/j.chemgeo.2014.07.018
0009-2541/

define the pressure–temperature windows where gold- and sulfur-bearing fluids are produced during an orogenic cycle (Tomkins, 2010; Gaboury, 2013; Pitcairn et al., 2014). A solubility limit on metal mobilization implies that fluid quantity, structural focusing of fluid flow and efficient mineral precipitation alone determine the ore-forming potential of metamorphic fluids (McCuaig and Kerrich, 1998; Phillips and Powell, 2009, 2010; Weatherley and Henley, 2013). By contrast, metal availability as the limiting factor would imply that the presence of pre-enriched source rocks in an orogenic terrain would favor the generation of anomalously gold-rich fluids and the formation of economic ore deposits.

Highly gold-enriched fluids have been discovered in upper-crustal magmatic–hydrothermal systems using trace-element analysis of fluid inclusions (Ulrich et al., 1999) and direct analysis of active geothermal fluids (Simmons and Brown, 2006). Anomalously gold-rich fluids may also occur in deeper metamorphic terrains, but representative regional-metamorphic fluid inclusions are difficult to relate to the formation of orogenic gold deposits due to the crustal-scale extent of these ore-forming systems (Groves, 1993), and because primary fluid inclusions are rare in regional metamorphic veins and their preservation is commonly questionable (van den Kerkhof and Hein, 2001; Bons et al., 2012). Fluid inclusions in economic gold vein deposit are usually diverse with numerous generations, they are difficult to relate to the stage of gold precipitation, and can at best be indirectly related to specific source rocks of the gold (Robert and Kelly, 1987; Ridley and Hagemann, 1999; Kerrich and Ludden, 2000; Pettke et al., 2000; Ridley and Diamond, 2000; Graupner et al., 2001; Uemoto et al., 2002; Garofalo, 2004; Duuring et al., 2007; Morelli et al., 2007; Neumayr et al., 2007; Saravanan et al., 2009; Yoo et al., 2010; Fu et al., 2012; Lawrence et al., 2013). The difficulty of identifying the primary metal-transporting ore fluids, together with analytical limitations, has led to unresolved contentions whether or not magmas or specialized source rocks are essential ingredients for orogenic gold ore formation in distinct periods of Earth's history (Goldfarb et al., 2001; Groves et al., 2003; Goldfarb et al., 2005; Duuring et al., 2007; Tomkins, 2010; Webber et al., 2013; Pitcairn et al., 2014).

In the present study, we have assessed the concentrations of gold and other ore metals in normal metamorphic fluids generated by prograde devolatilization of an orogenic belt. The Central Alps are an excellent field example because they expose well-preserved late-metamorphic fissure veins along a prograde facies series from subgreenschist- to amphibolite-grade, without any overprint by later tectono-metamorphic events (Poty et al., 1974; Mullis et al., 1994; Todd and Engi, 1997; Frey and Ferreiro Mählmann, 1999). We report the composition of fluid inclusions from 8 veins (Thusis, Vals, Gauli, Gerstenegg, Tiefengletscher, Bedretto, Cavagnoli, Faido; Fig. 1), determined by microthermometry and LA-ICPMS microanalysis, including the concentrations of Cu, Zn, Pb, Ag and Au. To overcome statistical problems with low concentrations near the limit of detection (LOD), we have developed a new method for the quantification of Au and other trace metals that is based on summation of the ICPMS signals of a population of single-inclusion measurements. We have compared the measured gold concentration data with results of thermodynamic fluid–mineral equilibria modeling in order to assess the saturation state of gold in the natural metamorphic fluids and to evaluate their ore potential.

2. Regional geology and vein–wall rock relationships

The Alps comprise a mixed package of granitoid basement, sedimentary cover rocks including accretionary wedge metasediments and subordinate oceanic crust, all interleaved in a complex nappe pile as a

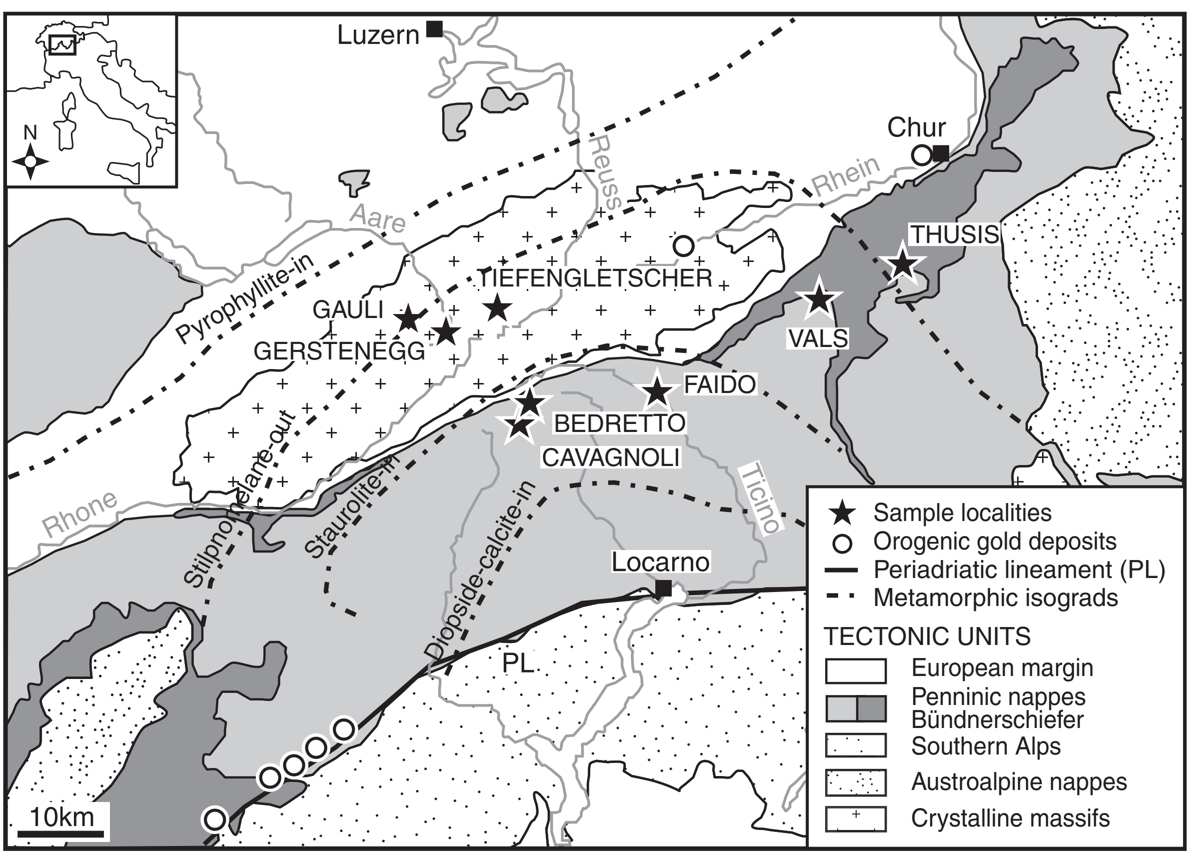

Fig. 1. Map of the Central Alps showing the major tectono-stratigraphic units of the collisional nappe complex (gray shades) between the European continent (white) and the partly overthrusted African or Adriatic plate (stippled), metamorphic isograds, the distribution of minor orogenic gold deposits and the location of sampled unmineralized veins on a prograde metamorphic section from sub-greenschist to amphibolite facies.