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Fate of gold and base metals during metamorphic devolatilization of a pelite

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Abstract

Scavenging of gold during metamorphic devolatilization is a widely accepted model for fluid and metal sourcing in orogenic gold deposits. In order to further constrain this process and quantify the capacity of autogenous fluids to release metals from pelites, we investigated the behaviors of S, Au, As, Cu, Pb, and Zn during pelite metamorphic devolatilization using thermodynamic modeling within the Al–As–Au–Cl–Cu–Fe–H–K–Mg–Na–O–Pb–S–Si–Ti–Zn system over a P–T range of 350–650 °C and 0.8–5 kbar.

The model revealed that S, Au and base metals are predominantly released via partitioning into the fluid phase during reactions that liberate H_2O: the dehydration of chlorite and muscovite, and to a lesser extent, the replacement of pyrite by pyrrhotite. Negligible sulfur is liberated during the pyrite–pyrrhotite transition, because the excess sulfur reacts with Fe in chlorite and muscovite to form pyrrhotite. The sulfidation of chlorite/muscovite releases water, so that a significant amount of Au can be liberated from S-rich pelites at the pyrite to pyrrhotite transition: up to 0.5 ppb Au (as a proportion of bulk rock) can be stripped from a pelite containing 1 wt.% sulfur, whereas only trace amounts of base metals can be mobilized under these conditions. Chlorite dehydration is the most important process in metal extraction; up to 2 ppb Au, 1.5 ppm Cu, 1 ppm Pb and 2 ppm Zn (as proportions of bulk rock) can be extracted from a pelite by autogenous fluids upon crossing the greenschist–amphibolite facies boundary. In comparison, an average pelite contains ~3 ppb Au, indicating that most Au within an average pelite can be scavenged as a result of the breakdown of chlorite.

Prograde metamorphism is an efficient mechanism for generating Au-bearing ore fluids: most Au can be extracted during chlorite dehydration from a source rock of average pelitic composition. In contrast, only a small portion of base metals can be released in autogenous fluids, and therefore only minor enrichment in base metals is expected within large orogenic gold deposits in metamorphic terrains, which is consistent with observations globally.

1. INTRODUCTION

Orogenic gold deposits account for more than a quarter of the World's Au resources (Goldfarb et al., 2005). A widely accepted genetic model proposes that Au is scavenged and collected by autogenous fluids during metamorphic devolatilization (Goldfarb et al., 2005; Phillips and Powell,

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2010; Tomkins, 2010), which is consistent with studies in the Southern Alps of New Zealand demonstrating the mobility of Au during regional metamorphism in an active orogen (Pitcairn et al., 2006, 2014). Yet, many fundamental aspects of the genesis of these deposits remain ambiguous. We modeled the complex interactions among native gold, Cu–Pb–Zn–Fe–As sulfides, Fe–Ti oxides, metamorphic silicate minerals and relevant solid solutions (biotite, chlorite, cordierite, garnet, muscovite, staurolite), and an aqueous fluid for a pelitic rock. By constraining the mechanism and efficiency of Au and base metal extraction during metamorphic devolatilization, this modeling contributes to answering the following three questions.

(i) The metamorphic devolatilization model is challenged by models involving externally derived fluid (and possibly Au) sources, including magmatic fluids (de Ronde et al., 2000), deeply convecting meteoric waters (Nesbitt et al., 1989), or mantle-derived fluids (Mao et al., 2008). These alternative models require external sources of fluids to extract Au from the source rocks. A key question to test the feasibility of the metamorphic devolatilization model is whether sufficient Au can be extracted from source rocks solely by internally generated metamorphic fluids.

(ii) Which reactions control Au extraction? Prograde metamorphism is characterized by a series of dehydration reactions involving breakdown of hydrous minerals (e.g., clay minerals, chlorite, and mica). During any of these reactions, some Au will be scavenged from the source rock into the fluid, but the amounts of Au liberated remain poorly constrained. The transition from pyrite to pyrrhotite during prograde metamorphism is also regarded as important for Au liberation, based on calculations within the Fe–S–O–H(–C) system suggesting that excess sulfur, the most important ligand for Au transport, will be liberated during the pyrite–pyrrhotite transition (Toulmin and Barton, 1964; Ferry, 1981; Tomkins, 2010), for example via the reaction:

$$FeS_2(\text{pyrite}) + H_2O = FeS(\text{pyrrhotite}) + H_2S(aq) + 1/2O_2(aq). \quad (1)$$

A shortcoming of these studies was the neglect of interactions between liberated sulfur and Fe minerals (Fe–Ti-oxides and Fe-silicates). Yet, these interactions are significant (Tracy and Robinson, 1988; Tomkins, 2007), even at low temperature (Qian et al., 2010). Understanding the Au extraction mechanisms gives insights into the temporal and spatial distribution of Au deposits in metamorphic terrains.

(iii) Another key question relates to the *gold-only* nature of orogenic Au deposits. Some researchers proposed that because Au forms strong complexes with S ligands, it is highly soluble in low salinity S-rich metamorphic fluids. In contrast, base metals such as Cu, Pb and Zn are primarily transported as chloride complexes, and therefore transported in subeconomic quantities in low-salinity metamorphic fluids (Phillips and Powell, 2010). Nevertheless, studies on some Cu (e.g., Zhong et al., 2012, 2013) and Pb–Zn deposits (e.g., Leach et al., 1988) revealed their metamorphic origin, although these deposits are sparse and of modest economic significance compared to orogenic Au deposits. Recent experimental studies revealed that some base metal hydrosulfide complexes are stable in high temperature fluids (e.g., Akinfiev and Zotov, 2010; Etschmann et al., 2010; Mei et al., 2013a), and therefore the mobility of base metals in low-salinity metamorphic fluids needs to be revisited.

2. DESCRIPTION OF THE MODEL

2.1. Overview

Thermodynamic equilibrium among minerals and an aqueous fluid was calculated using the HCh program, which is one of the few codes that calculate equilibrium among pure minerals, solid solutions, and a complex aqueous electrolyte solution (Shvarov and Bastrakov, 1999). Calculations were carried out within the Al–As–Au–Cl–Cu–Fe–H–K–Mg–Na–O–Pb–S–Si–Ti–Zn system over a *P*–*T* range of 350–650 °C and 0.8–5 kbar. About 4–8 wt.% NaCl was added in the aqueous phase by fixing the saturation level of halite at 0.01 in order to simulate the characteristic low-salinity of metamorphic fluids (Goldfarb et al., 2005).

The bulk composition of a 'typical pelite' from White et al. (2001) was used for the primary modeling, with addition of Fe(III) and Ti in the system to constrain the redox states. The FeO/Fe_2O_3 and FeO/TiO_2 ratios used are based on a weakly oxidized pelite reported by White et al. (2000). In addition, minor pyrite, native gold, sphalerite, galena and chalcopyrite were included in the starting composition, since pelites commonly contain minor quantities of pyrite with traces of Au, As, Zn, Pb, Cu and other key elements commonly found in orogenic gold systems (Large et al., 2009).

To monitor the influence of sulfur content (occurring mainly as pyrite in low-grade pelites) in metal extraction, the bulk composition of a sulfur-enriched pelite (1 wt.% S, Tomkins, 2010; i.e., (in mol%) $K_2O = 2.59$, $FeO = 5.71$, $FeO_{1.5} = 0.54$, $MgO = 3.28$, $Al_2O_3 = 8.06$, $SiO_2 = 67.65$, $TiO_2 = 0.494$, $Au = 0.00001$, $ZnS = 0.01$, $PbS = 0.01$, $CuFeS_2 = 0.01$, $FeS_2 = 0.487$) as well as a pelite with average sulfur content (~0.24 wt.% S; i.e., $FeS_2 = 0.116$ mol%) are used as starting materials. At low concentrations the sulfur content has minor influence on silicate metamorphic reactions, but the width of the pyrite–pyrrhotite coexistence field increases with increasing sulfur content (see Toulmin and Barton, 1964; Fig. 1), in accordance with the modeling of S-bearing metabasalt using THERMOCALC (Evans et al., 2010). In natural pelites, arsenic is mostly distributed as a trace element in pyrite, and therefore arsenopyrite is treated as an end member in the solid solution of As-pyrite. The mobility of As was investigated by fixing the activity of arsenopyrite as 1 and 0.01, respectively. A secondary model examined the effects