Thallium geochemistry in the metamorphic Lengenbach sulfide deposit, Switzerland: Thallium-isotope fractionation in a sulfide melt

KAI HETTMANN¹, KATHARINA KREISSIG², MARK REHKÄMPER², THOMAS WENZEL^{1,*}, REGINA MERTZ-KRAUS³ AND GREGOR MARKL¹

¹Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Wilhelmstrasse 56, 72074 Tübingen, Germany ²Department of Earth Science and Engineering, Imperial College London, U.K. ³Institut für Geowissenschaften, Johannes Gutenberg-Universität Mainz, Germany

ABSTRACT

The Lengenbach (Switzerland) Pb-As-Tl-Zn deposit was formed from a sulfide melt at about 500 °C during Alpine metamorphism, but details on its formation and especially the source of the metals are still under debate. In this study we present two sample sets to address these questions:

(1) MC-ICP-MS analyses of thallium isotopes in sulfides, sulfosalts, and melt inclusions from the Alpine metamorphic Lengenbach deposit in the Binn Valley of Switzerland, the non-metamorphic Wiesloch Mississippi Valley-type deposit in Southern Germany, and the Cu- and As-rich mineralization at Pizzo Cervandone about 2 km SW of the Lengenbach deposit, which has been discussed as potential source of the Lengenbach metals.

(2) LA-ICP-MS analyses of micas from the Lengenbach deposit and surrounding country rocks between the deposit and the Pizzo Cervandone to trace potential metal-bearing fluid pathways.

We found that Tl isotope compositions expressed as ε^{205} Tl values in all investigated samples range from -4.1 ± 0.5 to +1.9 ± 0.5. The whole variation can be seen in the Lengenbach deposit alone, which hence records considerable fractionation even during high-temperature processes involving a sulfide melt. This large range of ε^{205} Tl is thought to be caused by nuclear volume-dependent fractionation. Interestingly, the common fahlores at Lengenbach behave differently from all other investigated sulfosalts: based on their heavy isotopic composition together with a low As/S-ratio, they do not seem to be crystallized from the sulfide melt, but are interpreted to have formed from hydrothermal fluids enriched in the heavy Tl isotopes. Although As mobilization in the gneisses and dolomites surrounding the Lengenbach deposit is evident based on secondary arsenites, no traces of such a country rock fluid could be found in fissure micas at Lengenbach. Hence, considerations involving K/Rb, Rb/Tl, As/S, and Pb/Tl ratios in the sulfides and micas imply that the element enrichment in the Lengenbach deposit is either pre-Alpine or related to peak metamorphism, but occurred definitely before mica growth at Lengenbach.

Keywords: Sulfide melt, thallium isotopes, metal sources, sulfosalts

INTRODUCTION

The Lengenbach Pb-As-Tl-Zn deposit (Binn Valley/Switzerland) is well known for the occurrence of rare Tl-bearing sulfosalts and sulfides (Giusca 1930; Graeser 1965, 1975; Hofmann and Knill 1996; Graeser et al. 2008). It is the type locality of 31 mineral species, 16 of which have only been described from here (Hofmann et al. 1993; Graeser et al. 2008). This mineralogical diversity has been investigated in numerous publications since its discovery in the 19th century (Giusca 1930; Graeser 1965, 1975; Graeser et al. 2008).

The Lengenbach deposit formed under participation of a sulfide melt generated during regional metamorphism (Hofmann 1994). This process has been involved even in the generation of some world-class deposits, such as Broken Hill in Australia (Sparks and Mavrogenes 2005; Tomkins et al. 2007). A sulfide melt is produced if metamorphic temperatures are high enough to melt a precursor sulfide mineralization. The required temperature depends on the primary mineral composition, the mineral assemblages and f_{02} . In the course of fractional crystallization of the sulfide melt (Tomkins et al. 2007), As and Tl behave as incompatible elements. They are strongly enriched in the remaining melt fraction from which minerals such as jordanite and dufrenoysite crystallize.

Although the Lengenbach deposit was the subject of many scientific investigations, details of its formation and especially the source of the metals are still under debate: both the formation by melting of a hypothetical precursor mineralization (under nearly closed system conditions) and an external elemental input were discussed in the literature (e.g., Graeser and Roggiani 1976; Hofmann and Knill 1996).

In this study, we determined the chemical and Tl isotopic composition of various Tl-bearing sulfosalts, sulfides, and micas from the Lengenbach quarry in the Lengenbach deposit. The un-

^{*} E-mail: thomas.wenzel@uni-tuebingen.de

usual diversity of Tl-bearing minerals at the Lengenbach quarry makes it an ideal target for the exploration of the potential use of the new analytical method of Tl isotope composition on ore deposits (Rehkämper and Halliday 1998). For comparison, we also analyzed the Cu-As mineralization in pre-Alpine gneisses of the Pizzo Cervandone south of the Lengenbach quarry and a Mississippi Valley-type deposit at Wiesloch, South Germany. Alpine mobilization of the Pizzo Cervandone mineralization has been invoked in models to explain the chemical inventory of the Lengenbach deposit (Graeser 1965; Graeser and Roggiani 1976), while the Wiesloch Mississippi Valley-type deposit has been considered as a non-metamorphic analog for the precursor mineralization of Lengenbach (Hofmann and Knill 1996; Pfaff et al. 2010). The main purpose of this study was to obtain new insight into the formation of the Lengenbach deposit and the behavior of Tl isotopes during sulfide melt formation and evolution. Mica fractions from various fissures in different host rocks in the Binn Valley were additionally investigated to reconstruct potential pathways of Tl-bearing fluids or interaction with a sulfide melt.

GEOLOGY

The Lengenbach deposit is located in southern Switzerland in the Penninic units of the Alpine realm (Hofmann and Knill 1996). It occurs in metamorphosed Triassic dolomites in the Binn Valley (Fig. 1). Peak metamorphic conditions were determined in the Steinental close to the Binn Valley as upper greenschist to lower amphibolite facies (around 500 to 520 °C and 6.5 to 7.5 kbar) at 28 Ma ago (Frey et al. 1974; Vance and O'Nions 1992; Hofmann and Knill 1996).

Mineralized Triassic dolomites are located between a basement of granitic gneisses of the Monte Leone nappe and the overlying Bündnerschiefer (Fig. 1). The pre-Alpine basement is built up by Permian metasediments and meta-volcanics, and pre-Permian orthogneisses. The Bündnerschiefer consist of metamorphosed carbonate-rich sandstones and marls deposited during the extension of the Penninic basin and intercalated metamorphosed basalts. The dolomites hosting the mineralization are interpreted to have formed as platform dolomites during the beginning of the Penninic extension (Hofmann and Knill 1996; Galster 2014).

Triassic dolomites occurring in the Binn Valley area can be subdivided into two strata, the Lengenbacher stratum and the Feldbacher stratum (Fig. 1), at which the position of the locality Balmen is unclear, but most probably a part of the Lengenbacher stratum. The dolomites hosting the Lengenbach deposit are located in the Lengenbacher stratum and have a thickness of about 240 m. The mineralized zone is located close to the crystalline basement (Graeser 1965, 1975; Hofmann and Knill 1996). The major part of the mineralization consists of stratabound layers containing up to 80 vol% pyrite and smaller layers of sphalerite and galenite (Hofmann and Knill 1996), all with various kinds of rare sulfosalts. These layers can be subdivided into a reduced zone, an As(III)-rich zone and an intermediate redox zone (in stratigraphic order). The reduced zone is characterized by the occurrence of pyrite, pyrrhotite, arsenopyrite, sphalerite, magnetite, biotite, and uraninite. The As(III)-rich zone is composed of pyrite, barite, sphalerite, baumhauerite, sartorite, orpiment, realgar, and other As-rich sulfosalts (see Table 1). In this zone,



FIGURE 1. Schematic geological profile through the Binn Valley, Switzerland, showing the location of the Lengenbach quarry and the Pizzo Cervandone deposit. Modified after Graeser and Roggiani (1976).

Pb-Tl-rich sulfide melt inclusions in quartz have been identified and discordant veinlets containing baumhauerite, sartorite, realgar, and dufrenoysite are found (Hofmann and Knill 1996). The intermediate redox zone consists of pyrite, barite, galena, sphalerite, jordanite, and other As-poor sulfosalts. In addition to these stratigraphically confined zones, mineral druses and open fissures containing a large number of euhedral sulfosalts (>50 different species) and micas have been identified (Hofmann et al. 1993; Graeser et al. 2008).

The formation of the Lengenbach deposit has been interpreted to be the result of a sulfide melt generated at Alpine peak metamorphic conditions (Hofmann 1994). This sulfide melt underwent fractional crystallization of sulfosalts such as jordanite, which resulted in the enrichment of As and Tl, and the depletion of Pb in the remaining melt fractions. This is shown by compositional trends of melt inclusions, namely the enrichment of As and the depletion of Pb (Hofmann 1994), and the succession of more As-rich minerals observed in the Lengenbach deposit. Early phases include, e.g., rathite and jordanite, and late phases include, e.g., baumhauerite and sartorite (Giusca 1930). In ad-

 TABLE 1.
 Chemical composition of uncommon minerals mentioned

 in the text
 Image: Composition of uncommon minerals mentioned

In the text	
Mineral	Formula
asbecasite	Ca ₃ TiAs ₆ Be ₂ Si ₂ O ₂₀
baumhauerite	Pb ₁₂ As ₁₆ S ₃₆
cafarsite	Ca _{5.9} Mn _{1.7} Fe ₃ Ti ₃ (AsO ₃) ₁₂ ·4–5H ₂ O
cervandonite-(Ce)	(Ce,Nd,La)(Fe ³⁺ ,Fe ²⁺ ,Ti,Al) ₃ O ₂ (Si ₂ O ₇) _{1-x+y}
	$(As^{3+}O_3)_{1+x-y}(OH)_{3x-3y}$
chalcopyrite	CuFeS ₂
dufrenoysite	Pb ₂ As ₂ S ₅
edenharterite	PbTIAs ₃ S ₆
fetiasite	(Fe ³⁺ ,Fe ²⁺ ,Ti ⁴⁺) ₃ (As ₂ O ₅)O ₂
gasparite-(Ce)	(Ce,REE)AsO ₄
giessenite	(Cu,Fe) ₂ Pb _{26.4} (Bi,Sb) _{19.6} S ₅₇
graeserite	$Fe_{4}^{3+}Ti_{3}As^{3+}O_{13}(OH)$
hatchite	AgTIPbAs ₂ S ₅
hutchinsonite	TIPbAs₅S₀
jordanite	Pb ₁₄ (As,Sb) ₆ S ₂₃
molybdenite	MoS ₂
orpiment	As ₂ S ₃
paraniite-(Y)	$(Ca,Y,Dy)_2Y(WO_4)_2(AsO_4)$
rathite	$Ag_2Pb_{12-x}TI_{x/2}As_{18+x/2}S_{40}$
realgar	AsS
sartorite	PbAs ₂ S ₄
tennantite	$Cu_6[Cu_4(Fe,Zn)_2]As_4S_{13}$

dition, the presence of a hydrothermal aqueous fluid during and after the crystallization of the sulfide melt was proposed to be responsible for the formation of mica and quartz in open fissures (Hofmann et al. 1993).

In addition to the Lengenbach deposit, samples from mineralized orthogneisses at Pizzo Cervandone in the Binn Valley area (Fig. 1) have been investigated in this study as they are thought to represent a possible metal source for Lengenbach (Graeser 1975). At Pizzo Cervandone, basement orthogneisses host a pre-Alpine Cu-As mineralization consisting of sulfide minerals (Graeser and Roggiani 1976; Guastoni et al. 2006) and Alpine veins with unusual arsenite minerals (e.g., cafarsite, asbecasite, cervandonite). The major sulfide mineral is fahlore (tennantite) that is associated with quartz and mica in centimeter-thick veins. Fahlore is partly altered to copper carbonates, and occurs with minor pyrite, chalcopyrite, and molybdenite. The Alpine fissures contain abundant arsenates, arsenites, phosphates, and fluorite (Graeser and Roggiani 1976). The most remarkable among these are cervandonite-(Ce), gasparite-(Ce), paraniite-(Y), cafarsite, asbecasite, and fetiasite, which have their type locality in the Binn area (Graeser and Roggiani 1976; Armbruster et al. 1988; Graeser et al. 1994; Demartin et al. 1994). The occurrence of arsenates and arsenites has been interpreted to be a result of the remobilization of the orthogneiss-hosted tennantite (Guastoni et al. 2006).

Samples from the Mississippi Valley-type deposit at Wiesloch were also included in our investigation since it can be regarded as a non-metamorphic equivalent of Lengenbach. The deposit at Wiesloch formed during the extension of the Upper-Rhine graben in Muschelkalk dolomites at temperatures of about 150 °C (Pfaff et al. 2010). The mineralization consists of calcite, dolomite, barite, sphalerite, galena, pyrite, and subordinate sulfosalts like the Tl-bearing hutchinsonite.

SAMPLES

We analyzed two sample sets in this study that are interconnected through the Lengenbach deposit: the first sample set comprises sulfides and melt inclusions from Lengenbach, the Pizzo Cervandone mineralizations, and the Wiesloch Mississippi Valley-type deposit in Southern Germany. These samples were analyzed for their Tl isotope composition. All samples from Lengenbach are hosted by dolomite. Jordanite occurs as massive aggregates in dolomite (intermediate redox zone, see above), whereas sartorite, edenharterite, and fahlore are isolated euhedral crystals grown in vugs of the As(III)-rich zone. Orpiment occurs as thin fissure covers (for more details see Graeser 1965, 1975; Hofmann and Knill 1996). Sulfide-melt inclusions investigated and described by Hofmann (1994) were investigated in our study.

Samples from the deposit at the Pizzo Cervandone include fahlores (see Table 2) found in granitic gneisses and the arsenite mineral asbecasite grown as euhedral-free crystals in fissures. The mode of occurrence of these minerals has been described by Graeser and Roggiani (1976).

Samples from Wiesloch include banded sphalerite (schalenblende) and massive galenite that have been investigated and described by Pfaff et al. (2010).

The second sample set involves various types of micas from fissures in different host rocks sampled all over the Binn Valley including the Lengenbach deposit (for details on every sample see Table 3). These micas were analyzed for their Tl concentrations. Most mica samples are muscovite (12), but one sample of biotite was also analyzed. The samples are from fissures hosted by granitic gneisses or by dolomite of the Lengenbacher and Feldbacher strata. The dolomite at Balmen could not clearly be attributed to one of these strata and will therefore be discussed separately. The micas used in this study occur together with a wide range of other minerals as follows (sample number of the mica fraction in parentheses):

Sulfides including pyrrhotite (Bin30) and galenite (Bin23); sulfosalts including jordanite (Bin19), arsenopyrite (Bin26), and tennantite (Bin20, Bin23); carbonates including dolomite (Bin21), calcite (Bin28), azurite, malachite (both Bin20), and synchisite (Bin25); and silicates including quartz (Bin22), chrysocolla (Bin23), talc (Bin21), stilbite (Bin28), tourmaline and allanite (both in Bin25). In addition, oxides such as magnetite (Bin24, B5108), hematite and rutile (B5108), the arsenites graeserite and asbecasite and native gold (all three in Bin26) are found together with some of the fissure micas.

ANALYTICAL METHODS

Electron microprobe analysis

The major element compositions of the sulfosalts (As, S, Tl, Mn, Sb, Bi, Cu, Ag, Zn, Pb, and Fe) and fissure micas (Na, K, Ca, Mg, Fe, Mn, Al, Ti, Cr, Si, F, and Cl) were determined quantitatively using a JEOL JXA-8900RL Superprobe at the Fachbereich Geowissenschaften, Universität Tübingen. For the sulfosalts we applied the same analytical conditions as Staude et al. (2010), the micas were analyzed at 15 kV and 20 nA.

Thallium isotope composition of sulfides, sulfosalts, and melt inclusions

For Tl isotope measurements, hand-picked samples were dissolved in aqua regia and subsequently evaporated and redissolved in concentrated HCl several times. Thallium was then separated from the sample matrix following an isotope analysis only version of the two-stage anion-exchange chromatography described by Baker et al. (2009). All isotope measurements were performed using the Nu Plasma HR multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Nu Instruments) at Imperial College London. A 5% aliquot was used to determine the Tl concentration of each sample and to determine concentration levels as well as to ensure separation from Pb had been achieved. Subsequently, individual matching reference solutions (with the same Pb and Tl concentrations) were prepared using the NIST SRM 981 Pb and NIST SRM 997 Tl reference solutions. The measured 205Tl/203Tl ratio of each sample was mass-bias corrected relative to the 208Pb/206Pb ratio of the Pb reference material NIST SRM 981 (Ketterer et al. 1991), which had been mixed to each sample as well as to the matching reference solutions. Based on data obtained for multiple analyses of many samples and the matching standards, uncertainties (2 S.D.) are typically $\pm 0.5 \epsilon^{205}$ Tl and better than ±0.7 £205Tl throughout (Table 4). Results of reference material analyses, which show excellent agreement with literature values, can also be found in Table 4.

Trace element composition of fissure micas

Trace element contents were determined on polished mineral separates using the laser ablation ICP-MS (LA-ICP-MS) facility at the Institut für Geowissenschaften, Universität Mainz, equipped with an ESI NWR 193 excimer laser system coupled to an Agilent 7500ce quadrupole ICP-MS. On each grain up to 4 spots were analyzed, 34 isotopes (including ⁷⁵As, ⁸⁵Rb, ²⁰³Tl, and ²⁰⁵Tl) were monitored although this study is focused on the concentration of Tl and the large ion lithophile elements (LILE), specifically Rb. We used a dwell time of 10 ms for each mass (except 50 ms for ²⁰³Tl and ²⁰⁵Tl). A single spot analysis consists of 20 s background, 40 s ablation, and 20 s wash out. A laser beam diameter of 50 µm was used and the pulse repetition rate was set to 10 Hz. Energy density during ablation was around 5 J/cm². Before and after about 30 spots on the samples, reference materials were analyzed, including the synthetic NIST SRM 610 as calibration

TABLE 2. Major Element Composition of various suitosaits norm Lengembach and Cervando	element composition of various sullosaits from Lengenbach and Cervand	rvanuon
--	---	---------

Mineral	Aineral Edenharterite				Hatchite	Fahlore						
Locality	Direc	Lengenbach	Diac	Din 4	Lengenbach	D:= 4	D: 2	D: 2	Lengel	nbacn Dia C	Die	Diar
Sample	BINO	BINO	BINO	BIN4	BIN4	BIN4	BINZ	BINZ	BINZ	BIU2	BIU2	BID2
[wt%]	24.04	25 72	21 51	16.10	16.22	16.11	10 70	20.02	10.00	20.21	10.02	10.76
AS c	24.94	25./3	21.51	16.19	16.23	10.11	19.79	20.03	19.89	20.21	19.83	19.76
с ТI	25.79	25.45	25.12	19.44	19.25	19.45	27.21 bdl	27.52	27.00	27.54 bdl	27.54 bdl	20.05 bdl
Mp	24.42	4.60 bdl	0.40 bdl	24.50 bdl	24.75 bdl	24.00 bdl	bdi	0.06 bdl	0.07 bdl	bdl	bdl	bdi
Sh	0.03	0.67	1 20	0.56	0.49	0.80	0.06	0.04	0.00	0.07	0.08	0.10
Bi	bdl	bdl	hdl	bdl	bdl	0.00 bdl	0.00	0.04	0.09	0.07	bdl	0.10
Cu	0.28	0.19	bdl	1 49	1 41	1 28	42.86	42 64	42 50	42.01	42 51	42 77
Aa	bdl	0.03	0.32	10.51	10.51	10.70	1.42	1.35	1.47	1.40	1.50	1.36
Zn	bdl	bdl	bdl	bdl	bdl	bdl	8.41	8.55	8.27	8.44	8.35	8.27
Pb	24.39	42.80	46.55	24.52	25.04	24.70	bdl	bdl	bdl	bdl	bdl	bdl
Fe	0.03	0.03	0.03	bdl	bdl	bdl	bdl	0.20	0.25	0.20	0.24	bdl
Total	98.68	99.69	99.14	97.25	97.68	97.82	99.75	100.21	99.70	99.67	99.86	99.12
[apfu]												
As	2.69	2.60	2.39	1.78	1.80	1.77	4.05	4 08	4 09	4.11	4 04	4 09
S	6	6	6	5	5	5	13	13	13	13	13	13
TI	0.97	0.18	0.26	0.99	1.01	1.00		0.00	0.01			
Mn	0.00											0.00
Sb	0.05	0.04	0.08	0.04	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01
Bi								0.00	0.01	0.00		0.00
Cu	0.04	0.03		0.23	0.22	0.20	12.26	12.15	12.21	11.96	12.10	12.40
Ag		0.00	0.02	0.80	0.81	0.82	0.20	0.19	0.21	0.20	0.21	0.20
Zn							1.97	2.00	1.95	1.97	1.95	1.96
Pb	0.95	1.56	1.87	0.98	1.01	0.98						
Fe	0.00	0.00	0.00					0.05	0.07	0.06	0.07	
(As+Sb)/S	0.46	0.44	0.41	0.36	0.37	0.37	0.31	0.31	0.32	0.32	0.31	0.32
As/Sb	50	63	29	47	54	33	545	794	355	463	398	312
Dh/Tl	0.00	0 00	717	0.09	1.00	0.09						
10/11	0.99	0.00	7.17	0.90	1.00	0.90						
Mineral		Jordanite			Sartorite			Sulfide melt			Fahlore	
Mineral Locality		Jordanite Lengenbach			Sartorite Lengenbach			Sulfide melt Lengenbach		(Fahlore Cervandone	
Mineral Locality Sample	Bin3	Jordanite Lengenbach Bin3	Bin3	Bin9	Sartorite Lengenbach Bin9	Bin9	Bin13	Sulfide melt Lengenbach Bin13	Bin13	Bin8	Fahlore Cervandone Bin7	Bin7
Mineral Locality Sample [wt%]	Bin3	Jordanite Lengenbach Bin3	Bin3	Bin9	Sartorite Lengenbach Bin9	Bin9	Bin13	Sulfide melt Lengenbach Bin13	Bin13	Bin8	Fahlore Cervandone Bin7	Bin7
Mineral Locality Sample [wt%] As	Bin3 8.90	Jordanite Lengenbach Bin3 8.78	Bin3 8.50	Bin9 23.01	Sartorite Lengenbach Bin9 25.56	Bin9 22.81	Bin13 27.14	Sulfide melt Lengenbach Bin13 28.04	Bin13 33.35	Bin8	Fahlore Cervandone Bin7 19.15	Bin7 19.34
Mineral Locality Sample [wt%] As S	Bin3 8.90 17.12	Jordanite Lengenbach Bin3 8.78 17.30	Bin3 8.50 17.42	Bin9 23.01 22.97	Sartorite Lengenbach Bin9 25.56 24.27	Bin9 22.81 23.19	Bin13 27.14 26.25	Sulfide melt Lengenbach Bin13 28.04 26.39	Bin13 33.35 27.90	Bin8 19.43 28.33	Fahlore Cervandone Bin7 19.15 27.49	Bin7 19.34 27.76
Mineral Locality Sample [wt%] As S TI	Bin3 8.90 17.12 0.12	Jordanite Lengenbach Bin3 8.78 17.30 0.15	Bin3 8.50 17.42 0.13	Bin9 23.01 22.97 0.27	Sartorite Lengenbach Bin9 25.56 24.27 0.59	Bin9 22.81 23.19 0.28	Bin13 27.14 26.25 5.04	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31	Bin13 33.35 27.90 18.00	Bin8 19.43 28.33 bdl	Fahlore Cervandone Bin7 19.15 27.49 bdl	Bin7 19.34 27.76 bdl
Mineral Locality Sample [wt%] As S TI Mn	Bin3 8.90 17.12 0.12 bdl	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl	Bin3 8.50 17.42 0.13 bdl	Bin9 23.01 22.97 0.27 bdl	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03	Bin9 22.81 23.19 0.28 bdl	Bin13 27.14 26.25 5.04 0.03	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03	Bin13 33.35 27.90 18.00 0.02	Bin8 19.43 28.33 bdl bdl	Fahlore Cervandone Bin7 19.15 27.49 bdl bdl	Bin7 19.34 27.76 bdl bdl
Mineral Locality Sample [wt%] As S TI Mn Sb	Bin3 8.90 17.12 0.12 bdl 1.55	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63	Bin3 8.50 17.42 0.13 bdl 2.06	Bin9 23.01 22.97 0.27 bdl 0.66	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87	Bin9 22.81 23.19 0.28 bdl 0.53	Bin13 27.14 26.25 5.04 0.03 0.60	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01	Bin13 33.35 27.90 18.00 0.02 0.32	Bin8 19.43 28.33 bdl bdl 0.29	Fahlore Cervandone Bin7 19.15 27.49 bdl bdl 0.32	Bin7 19.34 27.76 bdl bdl 0.33
Mineral Locality Sample [wt%] As S TI Mn Sb Bi	Bin3 8.90 17.12 0.12 bdl 1.55 0.05	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl	Bin3 8.50 17.42 0.13 bdl 2.06 bdl	Bin9 23.01 22.97 0.27 bdl 0.66 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11	Bin9 22.81 23.19 0.28 bdl 0.53 bdl	Bin13 27.14 26.25 5.04 0.03 0.60 bdl	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl	Bin13 33.35 27.90 18.00 0.02 0.32 bdl	Bin8 19.43 28.33 bdl bdl 0.29 1.38	Fahlore Cervandone Bin7 19.15 27.49 bdl bdl 0.32 1.20	Bin7 19.34 27.76 bdl 0.33 1.07
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl bdl	Bin9 22.81 23.19 0.28 bdl 0.53 bdl bdl	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 0.22	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10	Fahlore Cervandone Bin7 19.15 27.49 bdl bdl 0.32 1.20 43.56	Bin7 19.34 27.76 bdl 0.33 1.07 43.67
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl bdl	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl bdl	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05	Bin9 22.81 23.19 0.28 bdl 0.53 bdl bdl 0.12	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl 0.22 bdl	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23	Bin7 19.34 27.76 bdl 0.33 1.07 43.67 0.24
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn	Bin3 8.90 17.12 bdl 1.55 0.05 bdl bdl 0.04	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl 0.02	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.12 bdl	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl bdl	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl bdl	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 0.24	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb C-	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl 0.02 69.84	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl bdl 49.80	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.12 bdl 50.35	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 41.34	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl 34.23	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.24	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 0.31	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.02
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total	Bin3 8.90 17.12 0.12 bdl 1.55 bdl 0.05 bdl 0.04 70.73 bdl 98.49	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl bdl 96.71	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.12 bdl 50.35 bdl 97.28	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 41.34 bdl 100.49	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl bdl 34.23 bdl 100.02	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl bdl 0.04 70.73 bdl 98.49	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl bdl bdl 0.02 69.84 0.04 97.75	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl bdl bdl bdl 0.06 69.82 0.04 98.03	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl 49.80 bdl 96.71	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 0.10 bdl 41.34 bdl 100.49	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl bdl 34.23 bdl 100.02	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Cu Ag Zn Pb Fe Total [apfu]	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl bdl 96.71	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 41.34 bdl 100.49	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl 34.23 bdl 100.02	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl bdl 0.02 69.84 0.04 97.75	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03 4.80	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 49.80 bdl 96.71	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl 19.17 bdl 98.99 0.51	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 12	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.02	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.22	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.02	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl 49.80 bdl 96.71 1.72 4 0.21	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02	Bin9 22.81 23.19 0.28 bdl 0.53 bdl bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.21	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.22	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.05	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 98.49 5.12 23 0.03	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl 96.71 1.72 4 0.01	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00	Bin9 22.81 23.19 0.28 bdl 0.53 bdl bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 41.34 bdl 100.49 0.44 1 0.03 0.00	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00	Bin13 33.35 27.90 18.00 0.02 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.00	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S S TI Mn	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl bdl 0.04 70.73 bdl 98.49 5.12 23 0.03	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 96.71 1.72 4 0.01	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 100.49 0.44 1 0.03 0.00 0.21	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 0.01 bdl bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn Sb Bi Bi Bi	Bin3 8.90 17.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 49.80 bdl 96.71 1.72 4 0.01 0.03 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S S TI Mn Sb Bi Cu	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl 49.80 bdl 96.71 1.72 4 0.01 0.03 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11 84	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12 33	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn Sb Bi Cu As	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl 49.80 bdl 96.71 1.72 4 0.01 0.03 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01 0.00	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn Sb Bi Cu As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl 96.71 1.72 4 0.01 0.03 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02 0.01	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01 0.00	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00	Bin8 19.43 28.33 bdl bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S S TI Mn Sb Bi Cu Ag S D Ei Cu Ag Pb Pb Pb Pb Pb Pb Pb Pb Pb Pb Pb Pb Pb	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03 14.70	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57 0.01 14.36	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72 0.04 14.26	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 96.71 1.72 4 0.01 0.03 0.00	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00 0.00 0.00 1.19	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02 0.01 1.34	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01 0.00	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00 0.00	Bin8 19.43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 43.16 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn Sb Bi Cu Ag S D Bi Cu Ag S Fe Total Pb Fe Fe	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03 14.70	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57 0.01 14.36 0.03	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72 0.04 14.26 0.03	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 96.71 1.72 4 0.01 0.03 0.00 1.34	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00 0.00 1.19	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02 0.01 1.34	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 100.49 0.44 1 0.03 0.00 0.01 0.00 0.24	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00 0.01 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00 0.00 0.11	Bin8 19,43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76 1.14	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82 1.12	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89 1.08
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S S Bi Cu Ag Zn Pb Fe Cu Ag Zn Pb Fe	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03 14.70	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57 0.01 14.36 0.03	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72 0.04 14.26 0.03 0.74	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl 49.80 bdl 96.71 1.72 4 0.01 0.03 0.00 1.34	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00 1.19	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02 0.01 1.34	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01 0.00 0.24	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00 0.20 0.00	Bin13 33.35 27.90 18.00 0.02 0.32 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00 0.00 0.11	Bin8 19,43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76 1.14	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82 1.12 0.30	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89 1.08 0.32
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S Bi Cu As S Bi Cu As S Fe Fe (As+Sb)/S	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03 14.70 0.25 9	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57 0.01 14.36 0.03 0.24 0.24 0	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72 0.04 14.26 0.03 0.24 7	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl 96.71 1.72 4 0.01 0.03 0.00 1.34 56	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00 1.19 0.46 48	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.12 bdl 50.35 bdl 97.28 1.68 4 0.01 0.02 0.01 1.34	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 41.34 bdl 100.49 0.44 1 0.03 0.00 0.01 0.00 0.24 0.45 74	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00 0.01 0.20 0.00 0.46 45	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00 0.00 0.11 0.51 169	Bin8 19,43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76 1.14 0.30 107	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82 1.12 0.30 97	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89 1.08 0.30 96
Mineral Locality Sample [wt%] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] As S TI Mn Sb Bi Cu Ag Zn Pb Fe Total [apfu] (As Sb Bi Cu As S S TI Mn Sb Sb Fe Total [As S S S S S S S S S S S S S S S S S S S	Bin3 8.90 17.12 0.12 bdl 1.55 0.05 bdl 0.04 70.73 bdl 98.49 5.12 23 0.03 0.55 0.01 0.03 14.70 0.25 9	Jordanite Lengenbach Bin3 8.78 17.30 0.15 bdl 1.63 bdl bdl 0.02 69.84 0.04 97.75 4.99 23 0.03 0.57 0.01 14.36 0.03 0.24 9	Bin3 8.50 17.42 0.13 bdl 2.06 bdl bdl 0.06 69.82 0.04 98.03 4.80 23 0.03 0.72 0.04 14.26 0.03 0.24 7	Bin9 23.01 22.97 0.27 bdl 0.66 0.00 bdl bdl bdl bdl bdl 96.71 1.72 4 0.01 0.03 0.00 1.34 0.44 56	Sartorite Lengenbach Bin9 25.56 24.27 0.59 0.03 0.87 0.11 bdl 0.05 bdl 46.52 bdl 97.98 1.80 4 0.02 0.00 0.04 0.00 0.04 0.00 1.19 0.46 48	Bin9 22.81 23.19 0.28 bdl 0.53 bdl 0.12 bdl 0.728 1.68 4 0.01 0.02 0.01 1.34 0.43 70	Bin13 27.14 26.25 5.04 0.03 0.60 bdl 0.10 bdl bdl 100.49 0.44 1 0.03 0.00 0.01 0.00 0.24 0.45 74	Sulfide melt Lengenbach Bin13 28.04 26.39 10.31 0.03 1.01 bdl 0.01 bdl bdl 34.23 bdl 100.02 0.45 1 0.06 0.00 0.01 0.00 0.01 0.20 0.00 0.46 45	Bin13 33.35 27.90 18.00 0.02 0.32 bdl 0.22 bdl bdl 19.17 bdl 98.99 0.51 1 0.10 0.00 0.00 0.00 0.11 0.51 169	Bin8 19,43 28.33 bdl 0.29 1.38 43.10 0.24 3.37 bdl 4.34 100.49 3.81 13 0.04 0.10 11.84 0.03 0.76 1.14 0.30 107	Fahlore Cervandone Bin7 19.15 27.49 bdl 0.32 1.20 43.56 0.23 3.54 bdl 4.11 99.61 3.88 13 0.04 0.09 12.33 0.03 0.82 1.12 0.30 97	Bin7 19.34 27.76 bdl bdl 0.33 1.07 43.67 0.24 3.88 bdl 4.03 100.31 3.88 13 0.04 0.08 12.24 0.03 0.89 1.08 0.30 96

material and NIST SRM 614, USGS BCR-2G, and GSD-1G as quality control materials (QCM). For data reduction we used the software GLITTER 4.0 (http:// www.glitter-gemoc.com) applying the preferred values for NIST SRM 610 reported in the GeoReM database (http://georem.mpch-mainz.gwdg.de/; Application Version 15, March 2013) (Jochum et al. 2005, 2011) as the "true" concentrations. All measured isotope intensities were normalized to ²⁹Si. SiO₂ contents applied for the

samples were previously determined by EMPA; for the QCM we used the preferred values of the GeoReM database. For BCR-2G, the current version of the GeoReM database reports no preferred value for TI. Therefore we applied as the "true" TI concentration the value determined recently by Nielsen and Lee (2013). For the QCM, relative standard deviation (RSD) for the averaged element concentrations of the single spot measurements was <17%, <6%, and <11% for NIST SRM 614

TABLE 3. Major and trace element composition of fissure micas, determined by EMPA and LA-ICP-MS, respectively

Mineral	Muscovite		te	Biotite Muscovite		Muscovite			Biotite				Muscovite					
Locality	Le	engenba	ngenbach I		Lengenbach		Gischi		Pizzo				Messerbach					
Host rock	Lenge	nbachers	acher stratum		Lengenbacher stratum		orthogneiss		orthoaneiss			Lengenbacher stratum						
Sample	5	Bin 18		Bin23 Bin16		Bin22			Bin20				Bin21					
[wt%]																		
F		0.41		2.80	0.	58		0.64			3	.41			0.	20		
Na₂O		0.33		0.24	0.35			0.22			0	.08			0.31			
K ₂ O		10.7		9.0	10).2		10.8			9	.47			11.0			
Cl		0.01		0.03	0.	02		0.01		bdl					0.01			
MgO		2.53		26.6	3.88			2.59		15.6					3.	.02		
CaO		bdl		bdl	0.	13		bdl			b	dl			0.	.03		
BaO		1.33		1.71	0.	42		0.04			b	dl			0.	21		
AI_2O_3		32.7		14.1	28	3.3		28.7			1	4.9			3	1.3		
MnO		bdl		bdl	0.	04		0.11			0	.42			b	dl		
TiO ₂		0.83		0.18	0.	75		0.28			0	.80			1.	.04		
SiO ₂		48.1		43.7	49	9.2		48.1			4	1.1			4	7.7		
FeO		bdl		0.13	0.	11		4.33			1	3.4			0.	29		
Cr_2O_3		0.05		bdl	1.	37		bdl			0	.03			0.03			
Total		97.0		98.5	95	5.3		95.9			9	9.1		95.1				
-F,CI=O		0.17		1.18	0.	25		0.27			1	.44		0.08				
H₂O		3.96		2.63	3.	82		3.74			2	.14		4.01				
Total		100.7		99.9	98	3.9		99.3			9	9.8			9	9.1		
[µg/g]																		
Li	418	427	404	548	240	224	763	762	1806	791	943	769	899	268	260	264	263	
As	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	9.94	28.8	74.9	20.9	56.7	bdl	bdl	bdl	bdl	
Rb	375	367	368	361	269	267	1554	1577	2534	1513	1330	1487	1272	293	259	310	261	
Sr	7.71	15.9	8.59	37.8	428	284	3.83	3.92	2.76	1.48	1.54	0.842	2.25	8.59	12.6	10.4	11.2	
Y	bdl	0.177	0.135	0.337	5.46	2.03	2.28	bdl	6.58	0.808	20.2	0.362	4.06	0.059	0.074	bdl	bdl	
Zr	bdl	0.176	0.151	bdl	0.330	1.12	0.390	0.406	bdl	bdl	0.231	bdl	bdl	0.259	0.387	0.326	0.580	
Nb	1.00	1.54	2.38	2.31	7.70	5.32	95.6	98.5	96.5	21.0	40.7	20.8	22.4	8.26	11.6	5.02	21.1	
Sn	28.8	34.7	45.6	4.23	6.75	8.68	392	408	108	94.8	102	94.9	85.0	10.4	13.3	8.46	18.4	
Sb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.730	0.670	1.41	0.500	1.98	bdl	bdl	bdl	2.01	
Cs	8.48	9.03	8.66	37.8	6.33	6.91	84.0	85.2	523	318	344	237	264	12.4	11.0	13.7	12.0	
La	0.026	bdl	bdl	0.670	17.4	6.79	0.434	bdl	0.554	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	
Ce	bdl	0.126	0.021	0.950	19.4	8.08	1.08	bdl	2.03	bdl	0.195	0.017	0.161	0.279	bdl	0.120	0.065	
Pr	bdl	bdl	bdl	0.141	1.74	0.930	0.179	bdl	0.213	0.017	0.068	bdl	0.024	bdl	bdl	0.021	bdl	
Nd	bdl	bdl	bdl	bdl	7.34	2.44	0.730	bdl	1.09	bdl	0.350	bdl	0.333	0.187	0.099	bdl	bdl	
Sm	bdl	bdl	bdl	bdl	1.29	bdl	bdl	bdl	0.260	0.056	bdl	bdl	0.237	bdl	bdl	bdl	bdl	
Eu	0.369	0.308	0.390	0.383	0.352	bdl	bdl	bdl	0.078	bdl	0.116	bdl	bdl	bdl	bdl	bdl	bdl	
Gd	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.720	bdl	1.01	bdl	bdl	bdl	bdl	bdl	bdl	
Tb	bdl	bdl	bdl	bdl	bdl	0.103	0.064	bdl	0.132	bdl	0.311	bdl	0.076	bdl	bdl	bdl	bdl	
Dy	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.31	bdl	3.24	bdl	0.520	bdl	bdl	bdl	bdl	
Ho	bdl	bdl	bdl	bdl	bdl	bdl	0.133	bdl	0.940	bdl	0.771	bdl	0.141	bdl	bdl	bdl	bdl	
Er	bdl	bdl	bdl	bdl	bdl	bdl	0.267	bdl	0.470	0.043	3.03	bdl	0.373	bdl	bdl	bdl	bdl	
Tm	bdl	bdl	bdl	bdl	bdl	bdl	0.054	bdl	0.098	bdl	0.519	bdl	0.097	bdl	bdl	bdl	bdl	
Yb	bdl	bdl	bdl	bdl	0.460	0.210	0.630	0.390	23.7	0.151	5.16	bdl	0.610	bdl	bdl	bdl	bdl	
Lu	bdl	bdl	bdl	bdl	bdl	bdl	0.179	0.189	0.070	0.018	0.606	0.018	0.133	bdl	bdl	bdl	bdl	
Ht T	0.219	0.050	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.038	bdl	0.115	bdl	bdl	bdl	
Ia	0.487	0.285	0.449	0.090	0.193	0.102	22.7	22.2	40.3	0.287	2.18	0.233	0.413	0.272	0.401	0.164	0.847	
TI	346	334	330	8.11	50.7	47.2	6.07	6.03	20.4	14.6	15.4	14.2	14.0	2.28	1.91	2.29	1.93	
Pb	3.52	1.19	2.88	49.9	21.2	42.1	7.52	8.59	171	30.0	44.1	17.6	102	5.20	5.82	14.0	9.01	
Ih	bdl	bdl	bdl	2.56	0.380	0.227	0.108	0.050	1.09	bdl	bdl	bdl	bdl	0.344	0.205	0.493	0.560	
U	bdl	0.027	0.014	0.098	0.950	0.187	0.181	bdl	3.31	0.528	0.872	0.126	1.24	bdl	bdl	bdl	bdl	

Continued on next page

(n = 9), GSD-1G (n = 9), and BCR-2G (n = 6), respectively. The element concentrations measured on the QCM (Appendix Table 1¹) agree within <13% with preferred values for most elements, but As (30% in GSD-1G), Sn (21% in GSD-1G and BCR-2G), and Tl (18% in NIST SRM 614). The difference between measured and true Tl concentration in NIST SRM 614 could be explained by analyses not only in the core region of the glass wafer but also closer to the rims. The rims have been reported to be depleted in some elements including Tl (Jochum et al. 2011).

During regular measurement conditions (sensitivities optimized for the full mass range), about 800 cps on ²⁰⁵Tl were measured per 1 µg/g Tl. For both Tl masses, background intensities are usually below 50 cps and relatively stable, resulting in minimum detection limits of about 0.2 µg/g. Isobaric interferences on the Tl masses appear to be of little importance, since the concentrations calculated from the intensities measured for ²⁰³Tl and ²⁰⁵Tl agree typically within 20% for Tl concentrations >0.2 µg/g and within 3% for Tl concentrations of >10 µg/g.

RESULTS

Chemical composition of the sulfides and sulfosalts from the Lengenbach deposit

The various samples from the Lengenbach deposit show a wide range of As concentrations (see Table 2) from 8.50 wt% in jordanite (Bin3) to 33.4 wt% in the sulfide melt inclusions (Bin13). This leads to molar (As+Sb)/S-ratios between 0.24 in jordanite to 0.51 in the sulfide melt inclusions (see Fig. 2a). The investigated samples also show a large range in Sb contents. The concentrations in the fahlore samples are low ranging from below the detection limit up to ~0.1 wt%. All other samples show higher contents from 0.32 wt% in the sulfide melt inclusions (Bin13) and up to >2 wt% in jordanite (Bin3). This leads to a broad range in molar As/Sb-ratios between 7 in jordanite (Bin3) and 169 in

¹ Deposit item AM-14-415, Appendix Table 1. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

TABLE 3.—CONTINUED	
--------------------	--

Musc	Muscovite Muscovite			Biotite			Muscovite			Muscovite				Biotite					
Gorb Gorb				Feldbach				Turtschi			Schin	horn		Ritterpass					
ortho	orthogneiss orthogneiss		Feldbacher stratum				Feldbacher stratum			orthogneiss			orthogneiss						
B5	108	Bin26				Bin	24			Bin30			Bin28				Bin25		
[wt%]																			
b	dl		0.12			1.1	15			0.07			0.0	04			1.54		
0.	26		0.63			0.0	07			0.52			0.2	21			0.06		
).9 -11		10.2			9.32			10.5				10	.9			9.45		
D 1	ai 71		2 00		0.01				bdl				bdl				DOI 15 7		
h.	/ I dl		bdl			b	4.9 41			2.90 bdl			h	41			hdl		
0	12		0.36			0.0)5			0.28			0.1	10			bdl		
30	0.0		32.0			13	.6			31.6			30	.5			16.0		
0.	04		bdl			b	dl			bdl			b	ll			0.65		
0.	96		0.68			0.3	30			0.53			0.0	30			1.45		
45	5.6		48.6			41	.2			49.0			46	.0			40.9		
5.	60		0.47			11	.6			0.43			5.5	50			12.5		
b	dl		bdl			b	ll			bdl			bo	ll			bdl		
95	5.1		96.1			97	.1			96.0			95	.6			98.3		
0.0	00		0.05			0.4	19 5			0.03			0.0)2			0.65		
4.0	00		4.11			3.4	25			4.13			4.0	0			3.09		
[ua/a]	9.1		100.1			99	.9			100.1			99	.0			100.7		
520	512	473	492	459	435	416	425	436	193	167	153	88.1	81.1	78.1	73.8	797	836 887		
bdl	12.2	40.2	79.6	19.7	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl bdl		
766	782	792	726	921	409	408	408	414	432	413	349	447	479	524	503	971	997 1006		
1.48	1.03	7.43	15.8	2.13	0.422	0.381	0.233	0.540	0.760	3.78	13.5	11.5	12.7	6.68	7.14	1.06	0.939 0.343		
bdl	0.130	17.6	40.5	1.39	0.053	bdl	bdl	bdl	bdl	0.280	1.49	bdl	bdl	bdl	bdl	2.74	5.44 0.350		
0.164	bdl	0.064	bdl	bdl	0.028	bdl	0.034	bdl	bdl	0.224	0.278	0.058	0.186	0.394	0.226	0.295	0.226 0.186		
44.4	42.1	53.3	47.2	50.2	24.1	24.6	24.7	24.7	28.8	27.6	34.5	15.6	31.6	30.10	63.0	250	263 182		
7.80	7.68	7.43	6.16	6.34	4.65	4.52	4.31	5.11	8.60	8.52	13.0	4.62	7.65	8.40	23.2	22.9	23.6 20.4		
2.57	1.87	3.95	4.15	4.23	0.650	120	0.820	0.940		0.77		DOI		0 77	bai	DOI 122	0.780 0.600		
bdl	0.057	68.1	116	1 10	hdl	bdl	hdl	hdl	9.00 bdl	9.77 bdl	0.37	hdl	bdl	bdl	bdl	125	121 130 20.8 1.08		
bdl	bdl	23.7	593	2.94	0.011	bdl	0.013	bdl	bdl	0.045	0.140	bdl	bdl	0.031	bdl	17.4	140 281		
bdl	bdl	12.5	23.5	0.813	bdl	bdl	bdl	bdl	0.012	bdl	0.075	bdl	bdl	bdl	bdl	2.81	6.24 0.272		
bdl	0.159	47.2	87.8	2.77	bdl	bdl	bdl	bdl	bdl	0.206	0.420	0.078	bdl	bdl	bdl	10.7	22.7 0.970		
bdl	bdl	5.73	12.6	0.400	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.68	3.34 0.183		
bdl	bdl	0.639	1.55	0.110	bdl	bdl	0.020	0.034	bdl	bdl	bdl	0.082	bdl	0.054	0.033	0.101	0.226 0.013		
bdl	bdl	4.17	7.16	0.316	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.980	3.14 bdl		
bdl	0.021	0.271	0.601	bdl	bdl	bdl	bdl	bdl	bdl	0.018	bdl	bdl	bdl	bdl	bdl	0.175	0.262 bdl		
bdl	bdl	1.53	3.38	bdl	bdl	bdl	bdl	bdl	bdl	0.130	0.364	bdl	bdl	bdl	bdl	0.540	1.22 bdl		
bdl	bdl	0.269	0.964	0.036	bdl	bdl	bdl	bdl	bdl	bdl	0.036	bdl	bdl	bdl	bdl	0.079	0.172 bdl		
bal	bdi	1.20	3.53	bdl	bdl	bdi	bdi	bal	bdi	bdi	bdl	bdi	bdi	bdl	bdi	0.212 bdl	0.385 DOI		
bdl	bdi	2.02	6 22	bdl	bdl	bdl	bdl	bdi	bdl	bdi	bdl	bdl	bdl	0.067	bdi	0 1 1 1	0.219 bdl		
bdl	0.014	0 394	1 1 2	0.040	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.034	0.056 bdl		
0.047	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.074	bdl	bdl	bdl	bdl	bdl	0.098	0.056	bdl	bdl 0.026		
3.84	4.09	3.08	3.19	3.51	1.17	1.21	1.27	1.26	3.02	2.75	3.60	0.728	1.46	0.452	2.12	13.5	14.0 10.6		
6.99	6.52	7.33	7.92	8.07	6.20	5.97	5.78	7.34	2.81	2.70	2.51	2.51	2.57	2.31	2.10	5.59	5.44 5.71		
3.94	5.60	27.5	42.2	16.4	6.82	4.89	6.66	11.0	0.269	1.22	2.96	6.04	9.11	3.73	3.79	4.22	3.73 1.50		
bdl	0.271	0.142	0.397	bdl	1.51	1.31	1.65	1.14	bdl	0.079	0.070	bdl	bdl	0.061	bdl	0.063	0.108 0.012		
28.4	0.063	1.69	0.558	0.023	0.088	0.062	0.086	0.444	bdl	0.110	bdl	bdl	0.017	bdl	bdl	1.13	1.19 0.225		

the sulfide melt inclusions (Bin13). Fahlores have even higher molar As/Sb-ratios between 312 (Bin5) and 794 (Bin2).

Some of the samples are rich in Pb and Tl. Pb contents reach up to 70 wt% in jordanite (Bin3). The highest concentration of Tl of 24.8 wt% was determined in hatchite (Bin4). However, some of the samples have Pb and Tl abundances below the detection limit (both ~200 μ g/g, depending on the minerals analyzed) and especially the fahlores do not show measurable contents of these elements. As a consequence, molar Pb/Tl-ratios, where they could be obtained, vary between 0.99 in edenharterite (Bin3) and 581 in jordanite (Bin6; see Fig. 2b).

The sulfosalts from the Lengenbach quarry show a large range in molar Tl/As-ratios. Fahlore samples have the lowest molar Tl/As-ratios of 0.001 (Bin2). Other sulfosalts have molar Tl/As-ratios ranging from 0.004 in sartorite (Bin9) to 0.56 in hatchite (Bin4).

The fahlore samples (Bin2 and Bin5) are tennantites with high Cu and Zn contents between 42.0 to 42.9 wt% and 8.23 to 8.55 wt%, respectively. The contents of Fe are low (between 0.17 and 0.25 wt%), while the Ag contents are rather high with concentrations between 1.32 and 1.59 wt%. No Bi could be detected in our samples (see Fig. 3b).

Chemical composition of the sulfide samples from Pizzo Cervandone

The fahlores of the Cu-As mineralization at Pizzo Cervandone are also tennantites (see Table 2). In addition to As and S, we could detect Cu, Fe, Zn, Ag, Bi, and Sb (see Fig. 3). The Cu contents are high and vary between 43.2 and 43.7 wt%, but Zn (3.54 to 3.88 wt%) and Ag contents (0.18 to 0.28 wt%) are low. Fe (3.89 to 4.13 wt%) and Bi (1.07 to 1.31 wt%) occur in significant concentrations. The contents of Sb are within a nar-

TABLE 4. Results of Tl isotope analysis

		· ·			
Reference	e materials		ε²٥₅ΤΙ	±2 S.D.	n
Aldrich Tl	this study		-0.8	0.6	3
	reference	/alue	-0.81	0.33	
AGV-2	this study		-3.6	0.6	3
	reference	/alue	-3.0	0.6	
Samples	Locality	Mineral	ε ²⁰⁵ Tl	±2 S.D.	n
Bin 1	Lengenbach quarry	jordanite	-4.1	0.5	2
Bin 2	Lengenbach quarry	fahlore	1.1	0.5	2
Bin 3	Lengenbach quarry	jordanite	-1.5	0.5	2
Bin 4	Lengenbach quarry	hatchite	0.6	0.5	1
Bin 5	Lengenbach quarry	fahlore	1.0	0.5	1
Bin 6	Lengenbach quarry	edenharterite	1.9	0.5	2
Bin 7	Pizzo Cervandone	fahlore	0.1	0.7	1
Bin 8	Pizzo Cervandone	fahlore	-3.0	0.6	1
Bin 9	Lengenbach quarry	sartorite	-2.2	0.5	2
Bin 10	Pizzo Cervandone	asbecasite	-2.0	0.5	1
Bin 11	Lengenbach quarry	orpiment	1.1	0.5	1
Bin 12	Lengenbach quarry	sartorite	-0.5	0.5	2
Bin 13	Lengenbach quarry	melt inclusions	-0.3	0.5	2
BG 186	Wiesloch	galenite	-1.4	0.5	1
BW114	Wiesloch	sphalerite	-2.7	0.5	1

Notes: n = number of individual analyses conducted on the same sample solution. The reference values for Aldrich TI and AGV-2 are from Nielsen and Rehkämper (2011).

row range between 0.30 and 0.33 wt%. This leads to low molar As/Sb-ratios between 94 and 104.

Trace elements in fissure micas

The Tl contents of dolomite-hosted micas (Table 3; Fig. 4) show a large variation from 1.91 μ g/g (Bin21) to 346 μ g/g (Bin18). Micas from the Feldbacher stratum (Bin24, Bin30) have relatively limited Tl concentrations between 2.51 μ g/g (Bin30) and 7.34 μ g/g (Bin24), and the sample from Balmen is characterized by a Tl abundance of 8.11 μ g/g (Bin23; see Fig. 4). In contrast, mica samples from the Lengenbacher stratum (Bin16, Bin18, Bin19, Bin21) are the most variable ones with regard to Tl concentrations (values from 1.91 to 346 μ g/g). Micas hosted by granitic gneisses are restricted to Tl contents between 2.10 μ g/g (Bin28) and 20.04 μ g/g (Bin22). Arsenic abundances are mostly below the detection limit, whereas concentrations can reach high levels up to 79.6 μ g/g in sample Bin26. All micas with measurable contents of As are from orthogneiss host rocks.

The Rb contents range from $259 \ \mu g/g$ (Bin21) to $2534 \ \mu g/g$ (Bin22). The concentrations of Rb show a continuum, but three groups can be distinguished based on their host rocks. Samples

◄ FIGURE 2. The composition of sulfosalts from the Lengenbach quarry. (a) Molar As/Sb vs. molar (As+Sb)/S; (b) molar Pb/Tl vs. molar (As+Sb)/S.





◆FIGURE 3. The composition of fahlore from the Lengenbach and the Pizzo Cervandone deposits. (a) Cu+Fe vs. Ag+Zn; (b) ternary molar composition in the As-Bi-Sb system.



FIGURE 4. Rb vs. Tl contents of fissure micas. Crustal Rb/Tl-ratios have been taken from Rudnick and Gao (2003).

hosted by Lengenbacher stratum dolomites generally show lower Rb contents (up to 375 μ g/g for Bin18) than the other samples hosted by dolomites. The samples hosted by dolomites have Rb contents between 349 and 432 μ g/g (both Bin30), these are lower than Rb concentrations in samples hosted by orthogneisses (>447 μ g/g in Bin25). The Cs contents show similar systematics: the samples from the dolomite of the Lengenbacher stratum have Cs concentrations between 6.33 μ g/g (Bin16) and 13.7 μ g/g (Bin21), whereas samples hosted by the Feldbacher stratum show Cs contents from 6.37 μ g/g (Bin30) to 142 μ g/g (Bin24). Micas hosted by granitic gneisses are also relatively rich in Cs (values from 6.82 μ g/g in Bin28 to 523 μ g/g in Bin22).

Isotope composition of Tl

The Tl isotope compositions were determined for 10 samples from Lengenbach, 3 from Pizzo Cervandone, and 2 from Wiesloch. These data (see Table 4) show a broad range of values between ε^{205} Tl = -4.1 (Bin1) and +1.9 (Bin6). Both extreme results are from samples of the Lengenbach deposit demonstrating the high variability within this deposit (Fig. 5). At Lengenbach, jordanite is the mineral species with the lightest isotope compositions between ε^{205} Tl = -4.1 and -1.5. One sartorite sample is isotopically heavier than jordanite, but another sartorite sample is slightly lighter with a value of ε^{205} Tl = -2.2. The other sulfosalts have higher values ranging from ε^{205} Tl = +0.6 to +1.9, while the sulfide melt inclusions shows $\varepsilon^{205}TI = -0.3$. The Tl isotope composition of the arsenite sample (asbecasite; ϵ^{205} Tl = -2.0) from the Cu-As mineralization at Pizzo Cervandone falls right in the range of the fahlore compositions from the same locality $(\epsilon^{205}Tl = -3.0 \text{ and } 0.1)$. The samples from the Wiesloch deposit show a smaller but still significant isotopic variability with ϵ^{205} Tl values between -1.4 and -2.7.

DISCUSSION

The formation of the Lengenbach deposit has been explained by melting of a stratabound precursor mineralization of preAlpine age (Hofmann 1994). The Alpine metamorphism caused the melting, and a subsequent fractional crystallization of the sulfide melt lead to the formation of the observed large variety of sulfosalts.

The assumption of a stratabound precursor mineralization is based on the observation that the mineralization in Lengenbach only occurs in metamorphosed Triassic dolomites. The association of dolomites with sulfide mineralization is typical of Mississippi Valley-type deposits known from several localities in Triassic dolomites such as, e.g., Bleiberg, Austria, and Meggen and Wiesloch, Germany (Gasser 1974; Gasser and Thein 1977; Schroll 1996; Pfaff et al. 2010).

The precursor mineralization and implications on external sources

The elemental inventory of the Mississippi Valley-type deposits mentioned above is rather similar to what is found in the Lengenbach deposit (Hofmann and Knill 1996). The Tl isotope composition of sulfides from the Wiesloch deposit (ϵ^{205} Tl of -1.4 and -2.7) is also isotopically similar to the composition of the Lengenbach deposit (Fig. 5). However, our data set is unfortunately too limited to draw the conclusion if an external elemental input has occurred.

Even if the elemental inventory of Lengenbach is similar to the deposits discussed above, typical Mississippi Valley-type deposits show lower As/Sb-ratios than the Lengenbach deposit (Hofmann and Knill 1996). This can be explained by the addition of As to the Lengenbach deposit by hydrothermal fluids before or during Alpine metamorphism (Graeser and Roggiani 1976). Arsenic could principally be derived from Cu-As mineralizations located in basement orthogneisses as, e.g., at Pizzo Cervandone. This model would also explain the high Cu contents of Lengenbach compared to Mississippi Valley-type deposits like Wiesloch. Mobilization of As at Pizzo Cervandone is corroborated by the abundant occurrence of As-bearing minerals in nearby Alpine fissures (Graeser and Roggiani 1976; Guastoni et al. 2006).

The ionic radii as well as the charge of Tl and Rb are very similar, which implies that the partitioning into mica is con-



FIGURE 5. The Tl isotope composition of various minerals from the Lengenbach quarry, Pizzo Cervandone, and the Wiesloch deposits.

stant. Therefore, Rb/Tl-ratios in micas can be used as proxy for the fluids crystallizing mica. However, based on the Rb-Tl systematics of micas both in host rocks, their fissures and in the Lengenbach deposit (Fig. 4), no influence of an external fluid can be discerned. Fissure micas of the mineralization in the Lengenbacher dolomite stratum have compositions different from all other analyzed mica samples with respect to Tl and Rb (Fig. 4). This can be explained if Lengenbach is considered as a closed system during this fluid activity. The fluid activity recorded in the fissure micas occurred at the time of or after fissure formation. Sulfide melts, such as at Lengenbach (Hofmann 1994) are dominated by the components of sulfosalts, which have low-solidus temperatures down to 300 °C (Tomkins et al. 2007). This is 200 °C lower than peak metamorphic temperatures in the Binntal area and it also means that the crystallization interval of the sulfide melt from liquidus to complete solidification is unusually large (>200 °C) (Tomkins et al. 2007). This 200 °C cooling from about 500 °C to about 300 °C probably took around 20 Ma (Challandes et al. 2008), which in turn had the effect that the melt could interact with hydrothermal fluids (e.g., with those present during the crystallization of the fissure micas). We propose that in this temperature interval, the fissures and their micas could be formed and hence could have reacted and equilibrated with the sulfide melt present in the rocks. In agreement with this statement, the fissure micas from the Lengenbach deposit show higher Tl contents than any other mica samples, indicating a very Tl-rich hydrothermal environment already during mica growth.

Based on the distinct and relatively low Rb/Tl-ratios of micas from the Lengenbach deposit (Fig. 4), we again conclude that either the precursor sulfide mineralization was already enriched in Tl or the enrichment took place under near-peak metamorphic conditions. Under peak metamorphic conditions the sulfide melt could have interacted with hydrothermal fluid and element scavenging could have effectively enriched the sulfide melt in Tl and As (Tooth et al. 2011). In contrast, fissure micas from dolomites of the Feldbacher stratum have higher concentrations of Rb than samples from the Lengenbacher stratum. The hydrothermal fluid responsible for the crystallization of the fissure micas might have been influenced by the Bündnerschiefer surrounding the Feldbacher dolomite stratum. Fissure micas from basement orthogneisses show Rb and Tl contents similar to granitic crustal rocks (Rudnick and Gao 2003). In these fissures, also the arsenite minerals occur recording the mobilization of the Pizzo Cervandone mineralization. Interestingly, and importantly, however, they do not record at all the presence of a Tl-rich hydrothermal fluid.

The Tl isotope composition of most minerals from the Lengenbach deposit is heavier than the average crustal value of ε^{205} Tl \approx -2 (Fig. 5; Nielsen et al. 2005, 2011). The only reservoir known to contain very heavy isotope compositions of Tl are marine ferromanganese (Fe-Mn) oxides (Rehkämper et al. 2002, 2004; Nielsen et al. 2009). In agreement with investigations of Hofmann and Knill (1996), sea floor oxides, such as Fe-Mn nodules, are among possible Lengenbach precursor rocks and hence they might have contributed to the element inventory of the deposit, although we admit that it is not typical to find such nodules on carbonate platforms. In addition, Fe-Mn oxides can be highly enriched in Tl (Rehkämper et al. 2002, 2004) and,

therefore, are able to exert a major control on the Tl budget of the Lengenbach deposit. The conclusion that marine Fe-Mn oxides can dominate the Tl budget of magmatic systems is in accordance with a previous study, which suggested that the relatively high ε^{205} Tl of some Hawaiian magmas is also a signature of such materials (Nielsen et al. 2006). As shown by Calvert and Price (1977) and by Neal et al. (1979), such sea-floor oxides also contain significant amounts of As and Cu. Accordingly, we propose that the precursor of the Lengenbach mineralization may have been chemically modified by the addition of Tl, Cu, and As from sea-floor fluids and related Mn-oxides. The only other source for Tl could be K- (and therefore Tl-) bearing minerals in the surrounding host rocks such as micas in the Bündnerschiefer or K-feldspar in the granitic gneisses.

Evidence from Tl isotope composition on the origin and mobilization of the Pizzo Cervandone mineralization

The Tl isotope composition of the mineralization at Pizzo Cervandone (Fig. 5) lies in the range previously determined for Cu porphyry deposits (Baker et al. 2010). This supports the interpretation of the magmatic origin of the Pizzo Cervandone mineralization as previously suggested by Graeser and Roggiani (1976). The isotopic composition of asbecasite from Alpine fissures at Pizzo Cervandone lies right in the middle of the range of the primary fahlores, indicating that a mobilization of "primary Tl" is assumed to have occurred during the Alpine metamorphism. However, the large range in the Tl isotopic composition of the primary minerals does not allow an evaluation of whether isotopic fractionation occurred during the alteration and mobilization process.

Chemical and isotopic fractionation of the sulfide melt

The range in the isotope composition of Tl within the Lengenbach deposit is 5 ε -units, which is large (Nielsen and Rehkämper 2011), especially for high-temperature processes (Schauble 2004). This large range can be theoretically explained by isotope fractionation during melt formation, during fractional crystallization of the ore minerals from the melt, or by the input of variable amounts of Tl from sources with different isotope compositions. During fractional crystallization, Tl and As are incompatible and enriched in the remaining melt fractions (Tomkins et al. 2007). This is also seen in the crystallization sequence of the Lengenbach deposit, where later As-rich minerals such as baumhauerite replace earlier As-poor phases such as, e.g., jordanite (Giusca 1930). Comparing molar Tl/As-ratios of the analyzed minerals with their Tl isotope composition, we observe the lightest isotope compositions in the samples with the lowest molar Tl/As-ratios, and vice versa for phases with heavier Tl isotope compositions (Fig. 6). This can be explained by the preferred incorporation of the lighter Tl isotope into the solid phase and an enrichment of the heavier isotope in the remaining sulfide melt if fractional crystallization is the most important process. In general, Tl isotope fractionation between sulfides or sulfosalts and a sulfide melt is thought to be small because S and As are the most important nearest structural neighbors in both cases. However, the structural arrangements (coordination and atomic distances) of these elements differ between minerals and melt, which might explain larger fractionation effects on

Tl isotopes [compare, e.g., Takeuchi and Sadanaga (1969) and Pohl (1982)]. Larger fractionation is more likely for partitioning between a sulfide melt and an aqueous fluid, because the chemical environments are very different. Thallium is transported as a chloride complex in saline fluids (Xiong 2007), whereas it is probably ionic in the melt. The presence of a saline aqueous fluid at Lengenbach during and after the presence of the sulfide melt has been detected by the occurrence of fluid inclusions in quartz (Hofmann and Knill 1996). Accordingly, an isotopic equilibrium between solids, sulfide melt and an associated aqueous fluid can be assumed. In this case, isotope fractionation can be considered as a fractionation between a bulk mobile phase (i.e., melt plus aqueous fluid) and the solids, since isotope compositions shift due to mass-balance in the whole system. This model requires that sulfides incorporate more light isotopes compared to the aqueous fluid, resulting in a heavier bulk isotope composition of sulfide melt and aqueous fluid. This scenario could explain most of the observed isotope variations.

The fahlores are the only minerals from the Lengenbach deposit, which do not follow the trend of increasing Tl/As-ratios with increasing ϵ^{205} Tl (Fig. 6). According to their Tl/As-ratio they should have crystallized at an early stage of the formation of the deposit. However, both the isotope composition of Tl and the As/Sb-ratios of the fahlores do not corroborate this (see Fig. 5). The isotope composition of Tl is among the heaviest found in the Lengenbach deposit suggesting a very late crystallization. The fact that fahlore falls off the general trend in the ϵ^{205} Tl vs. molar Tl/As-ratios diagram (Fig. 6) may reflect either that fahlore crystallization occurred after the sulfide melt had solidified, while hydrothermal activity persisted at lower temperature, or it may be a hint that indeed various metal sources contributed to the formation of the deposit.

Except for fahlore at Lengenbach, all of our results can be explained by Tl isotope fractionation occurring during fractional crystallization of a sulfide melt in equilibrium with an aqueous fluid.

However, temperatures between 300 and 500 °C are very high for isotope fractionation of heavy elements such as Tl and



FIGURE 6. Thallium isotope composition of sulfosalts from the Lengenbach quarry plotted vs. molar Tl/As-ratios.

cannot be caused by mass-dependent fractionation, which is very low at high temperatures (Bigeleisen and Mayer 1947). In contrast, nuclear volume-dependent or kinetic processes can cause significant fractionation at high temperatures. Nuclear volumedependent fractionation is much stronger for heavy elements at high temperatures (Schauble 2007) and kinetic fractionation can be caused by differences in the activation energies of ongoing reactions. However, kinetic fractionation depends on the differences of ionic properties between the isotopes or on diffusivity in high-temperature processes (Schauble 2004). Since the mass difference is small and diffusivity is rapid in sulfide melts (Majewski and Walker 1998), this process probably is minor, unless unknown kinetic effects take place.

IMPLICATIONS

Our study shows that crystallization of a sulfide melt can cause fractionation of heavy elements, as exemplified by Tl. Therefore, the isotopic analysis of high-temperature mineral deposits can be used to reconstruct the trace element distribution in a metamorphic environment where sulfide melts form. The crystallization products of metamorphic sulfide melts form world-class mineral deposits, and isotopic investigations of additional examples of these might give further hints on their generation and the processes involved.

ACKNOWLEDGMENTS

We thank T. Raber, S. Graeser, and B. Hofmann for providing sample material, and I. Gill-Kopp for sample preparation. Financial support of this study has been provided by the Landesgraduiertenförderung Baden-Württemberg to Kai Hettmann. We also thank S. Nielsen and J. Brugger for their constructive reviews, which helped to improve this manuscript.

REFERENCES CITED

- Armbruster, T., Bühler, C., Graeser, St., Stalder, H.A., and Amthauer, G. (1988) Cervandonite-(Ce), (Ce,Nd,La)(Fe³⁺,Fe²⁺,Ti⁴⁺,Al)₃SiAs(Si,As)O₁₃, a new Alpine fissure mineral. Schweizerische Mineralogische und Petrographische Mitteilungen, 68, 125–132.
- Baker, R.G.A., Rehkämper, M., Hinkley, T.K., Nielsen, S.G., and Toutain, J.P. (2009) Investigation of thallium fluxes from subaerial volcanism—implications for the present and past mass balance of thallium in the oceans. Geochimica et Cosmochimica Acta, 73, 6340–6359.
- Baker, R.G.A., Rehkämper, M., Ihlenfeld, C., Oates, C.J., and Coggon, R. (2010) Thallium isotope variations in an ore-bearing continental igneous setting: Collahuasi Formation, northern Chile. Geochimica et Cosmochimica Acta, 74, 4405–4416.
- Bigeleisen, J., and Mayer, M.G. (1947) Calculation of equilibrium constants for isotopic exchange reactions. Journal of Chemical Physics, 15, 261–267.
- Calvert, S.E., and Price, N.B. (1977) Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean. Marine Chemistry, 5, 43–74.
- Challandes, N., Marquer, D., and Villa, I.M. (2008) P-T-t modelling, fluid circulation, and 39Ar-40Ar and Rb-Sr mica ages in the Aar Massif shear zones (Swiss Alps). Swiss Journal of Geosciences, 101, 269–288.
- Demartin, F., Gramaccioli, C.M., and Pilati, T. (1994) Paraniite-(Y), a new tungstate arsenate mineral from Alpine fissures. Schweizerische Mineralogische und Petrographische Mitteilungen, 74, 155–160.
- Frey, M., Hunziker, J.C., Frank, W., Bocquet, J., Dal Piaz, G.V., Jäger, E., and Niggli, E. (1974) Alpine metamorphism of the Alps. A review. Schweizerische Mineralogische und Petrographische Mitteilungen, 54, 247–290.
- Galster, F., Cavargna-Sani, M., Epard, J-L., and Masson, H. (2014) New stratigraphic data from the Lower Penninic between the Adula nappe and the Gotthard massif and consequences for the tectonics and the paleogeography of the Central Alps. Tectonophysics, in press.
- Gasser, U. (1974) Zur Struktur und Geochemie der stratiformen Sulfidlagerstätte Meggen (Mitteldevon, Rheinisches Schiefergebirge). Geologische Rundschau, 63, 52–73.
- Gasser, U., and Thein, J. (1977) Das syngenetische Sulfidlager Meggen im Sauerland (Struktur, Geochemie, Sekundärdispersion). Forschungsbericht des Landes Nordrhein-Westfalen No. 2620/Fachgruppe Chemie. Westdeutscher

Verlag, 171 pp. (in German).

- Giusca, D. (1930) Die Erze der Lagerstätte vom Lengenbach im Binnental (Wallis). Schweizerische Mineralogische und Petrographische Mitteilungen, 10, 152–177 (in German).
- Graeser, S. (1965) Die Mineralfundstellen im Dolomit des Binnatales. Schweizerische Mineralogische und Petrographische Mitteilungen, 45, 597–795 (in German).
- (1975) Die Mineralfundstelle Lengenbach, Binntal. Schweizerische Mineralogische und Petrographische Mitteilungen, 55, 143–149 (in German).
- Graeser, S., and Roggiani, A.G. (1976) Occurrence and genesis of rare arsenate and phosphate minerals around Pizzo Cervandone, Italy/Switzerland. Rendicontri della Societa Italiana di Mineralogia e Petrologia, 32, 279–288.
- Graeser, S., Schwander, F., Gramaccioli, C.M., Pilati, T., and Reusser, E. (1994) Fetiasite (Fe²⁺, Fe³⁺, Ti)₃O₂[As₂O₃], a new arsenite mineral; its description and structure determination. American Mineralogist, 79, 996–1002.
- Graeser, S., Cannon, R., Drechsler, E., Roth, P., and Raber, T. (2008) Faszination Lengenbach, Abbau–Forschung–Mineralien (1958–2008). Kristallografik Verlag, Achberg (in German).
- Guastoni, A., Pezzota, F., and Vignola, P. (2006) Characterization and genetic inferences of arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn from Mount Cervadone (Western Alps, Italy). Periodico di Mineralogia, 75, 141–150.
- Hofmann, B. (1994) Formation of a sulfide melt during Alpine metamorphism of the Lengenbach polymetallic sulfide mineralization, Binntal, Switzerland. Mineralium Deposita, 29, 439–442.
- Hofmann, B., and Knill, M.D. (1996) Geochemistry and genesis of the Lengenbach Pb-Zn-As-Tl-Ba-mineralisation, Binn Valley, Switzerland. Mineralium Deposita, 31, 319–339.
- Hofmann, B., Graeser, S., Imhof, T., Sicher, V., and Stalder, H.A. (1993) Mineralogie der Grube Lengenbach, Binntal, Wallis. Jahrbuch des Naturhistorischen Museums Bern, 11, 3–90 (in German).
- Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., and Hofmann, A.W. (2005) GeoReM: A new geochemical database for reference materials and isotopic standards. Geostandards and Geoanalytical Research, 29, 333–338.
- Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Günther, D., and Enzweiler, J. (2011) Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines. Geostandards and Geoanalytical Research, 35, 397–429.
- Ketterer, M.E., Peters, M.J., and Tisdale, J. (1991) Verification of a correction procedure for measurement of lead isotope ratios by Inductively Coupled Plasma Mass Spectrometry. Journal of Analytical Atomic Spectrometry, 6, 439–443.

Majewski, E., and Walker, D. (1998) S diffusivity in Fe-Ni-S-P melts. Earth and Planetary Science Letters, 160, 823–830.

- Neal, C., Elderfield, H., and Chester, R. (1979) Arsenic in sediments of the North Atlantic Ocean and the Eastern Mediterranean Sea. Marine Chemistry, 7, 207–219.
- Nielsen, S.G., and Lee, C.-T.A. (2013) Determination of thallium in the USGS Glass Reference Materials BIR-1G, BHVO-2G and BCR-2G and application to quantitative Tl voncentrations by LA-ICP-MS. Geostandards and Geoanalytical Research, 37, 337–343, DOI: 10.1111/j.1751-908x.2012.00203.x.
- Nielsen, S.G., and Rehkämper, M. (2011) Thallium isotopes and their application to problems in Earth and environmental science. In P. Fritz and J.C. Fontes, Eds., Handbook of Environmental Isotope Geochemistry, p. 247–269. Springer, Berlin.
- Nielsen, S.G., Rehkämper, M., Porcelli, D., Andersson, P., Halliday, A.N., Swarzenski, P.W., Latkoczy, C., and Günther, D. (2005) Thallium isotope composition of the upper continental crust and rivers—An investigation of the continental sources of dissolved marine thallium. Geochimica et Cosmochimica Acta, 19, 2007–2019.
- Nielsen, S.G., Rehkämper, M., Norman, M.D., Halliday, A.N., and Harrison, D. (2006) Thallium isotopic evidence for ferromanganese sediments in the mantle

source of Hawaiian basalts. Nature, 439, 314-317.

- Nielsen, S.G., Mar-Gerrison, S., Gannoun, A., LaRowe, D., Klemm, V., Halliday, A.N., Burton, K.W., and Hein, J.R. (2009) Thallium Isotope evidence for increased marine organic carbon export in the Early Eocene. Earth and Planetary Science Letters, 278, 297–307.
- Pfaff, K., Hildebrandt, L.H., Leach, D.L., Jacob, D.E., and Markl, G. (2010) Formation of the Wiesloch Mississippi Valley-type Zn-Pb-Ag deposit in the extensional setting of the Upper Rhinegraben, SW Germany. Mineralium Deposita, 45, 647–666.
- Pohl, K.D. (1982) Orientation birefringence and structure of sulfur and arsenic sulfide melts. Physics and Chemistry of Glasses, 23, 23–30.
- Rehkämper, M., and Halliday, A.N. (1998) The precise measurement of Tl isotopic compositions by MC-ICPMS: Application to the analysis of geological materials and meteorites. Geochimica et Cosmochimica Acta, 63, 935–944.
- Rehkämper, M., Frank, M., Hein, J.R., Porcelli, D., Halliday, A.N., Ingri, J., and Liebetrau, V. (2002) Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits. Earth and Planetary Science Letters, 197, 65–81.
- Rehkämper, M., Frank, M., Hein, J.R., and Halliday, A.N. (2004) Cenozoic marine geochemistry of thallium deduced from isotopic studies of ferromanganese crusts. Earth and Planetary Science Letters, 219, 77–91.
- Rudnick, R.L., and Gao, S. (2003) The composition of the continental crust. In R.L. Rudnick, Ed., The Crust, 3, p. 1–64. Treatise on Geochemistry (H.D. Holland and K.K. Turekian, Exec. Eds.), Elsevier-Pergamon, Oxford.
- Schauble, E. (2004) Applying stable isotope fractionation theory to new systems. In C.M. Johnson, B.L. Beard, and F. Albarede, Eds., Geochemistry of Non-Traditional Stable Isotopes, 55, p. 65–111. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.
- Schauble, E.I. (2007) Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. Geochimica et Cosmochimica Acta, 71, 2170–2189.
- Schroll E. (1996) The Triassic carbonate-hosted Pb-Zn mineralization in the Alps (Europe): The genetic position of Bleiberg type deposits. In D.F. Sangster, Ed., Carbonate-Hosted Lead-Zinc Deposits, 4, p. 182–194. Society of Economic Geology Special Publications, Littleton, Colorado.
- Sparks, H.A., and Mavrogenes, J.A. (2005) Sulfide melt inclusions as evidence for the existence of a sulfide partial melt at Brocken Hill, Australia. Economic Geology, 100, 773–779.
- Staude, S., Mordhorst, T., Neumann, R., Prebeck, W., and Markl, G. (2010) Compositional variation of the tennantite-tetrahedrite solid-solution series in the Schwarzwald ore district (SW Germany): The role of mineralization processes and fluid source. Mineralogical Magazine, 74, 309–339.
- Takeuchi, Y., and Sadanaga, R. (1969) Structural principles and classification of sulfosalts. Zeitschrift für Kristallographie, 130, 346–368.
- Tomkins, A.G., Pattison, D.R.M., and Frost, B.R. (2007) On the initiation of metamorphic sulfide anatexis. Journal of Petrology, 48, 511–535.
- Tooth, B., Ciobanu, C., Neil, B., Green, L., and Brugger, J. (2011) Bi-melt formation and Gold scavening from hydrothermal fluids: An experimental study. Geochimica et Cosmochimica Acta, 75, 5423–5443.
- Vance, D., and O'Nions, R.K. (1992) Prograde and retrograde thermal histories from the central Swiss Alps. Earth and Planetary Science Letters, 114, 113–129.
- Xiong, Y. (2007) Hydrothermal thallium mineralization up to 300 °C: A thermodynamic approach. Ore Geology Reviews, 32, 291–313.

MANUSCRIPT RECEIVED MAY 7, 2013 MANUSCRIPT ACCEPTED NOVEMBER 11, 2013 MANUSCRIPT HANDLED BY RICHARD WILKIN