THE JABALI, HAKKARI AND REEF RIDGE NONSULFIDE Zn(Pb) DEPOSITS: AN EVALUATION BY QEMSCAN® TECHNOLOGY, AND COMPARISON TO OTHER ANALYTICAL METHODS

LICIA SANTORO
Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università "Federico II", Via Mezzocannone 8, 80134 Napoli

INTRODUCTION AND AIMS OF THE WORK

Supergene Zn(Pb)-nonsulfide deposits consist mainly of Zn/Pb-carbonates (smithsonite, hydrozincite, cerussite), Zn-(hydro)silicates (hemimorphite, sauconite), Fe-(hydr)oxides, minor Fe/Pb-sulfates (*i.e.* anglesite, jarosite) and Zn/Pb-phosphates (*i.e.* tarbuttite, pyromorphite), commonly associated with remnants of primary sulfides (sphalerite and galena), which form from oxidation of sulfide-bearing ores by meteoric waters (Large, 2001; Hitzman *et al.*, 2003; Boni & Mondillo, 2015). The relative abundances of these mineral phases and the precipitating mineral species are strongly dependent on the type of host rock. Their variable mineralogy is complex to characterize, and it is crucial to define the processing method and foresee the metal recovery. Since most nonsulfide Zn-Pb deposits are amenable to be treated by hydrometallurgy, *e.g.* by leach/solvent extraction/electrowinning, AmmLeach®, etc. (Bodas, 1996; Abdel-Aal, 2000; Loan *et al.*, 2006; Souza *et al.*, 2007; de Wet & Singleton, 2008), an incorrect evaluation of the modal distribution, or of the relations between ore and gangue minerals, could lead to a severe increase of the production costs or drive the choice of the processing route in erroneous directions (Santoro *et al.*, 2014).

Objective of this thesis, hence, was to integrate the more traditional analytical technologies (OM, CL, SEM-EDS, WDS, and CA) with the "Automated Mineralogy" analysis system (QEMSCAN®), in order to improve the accuracy of nonsulfide ores characterization. Part of this aim has been reached by the comparison of the quantitative evaluation of three supergene nonsulfide deposits, carried out with two different methods: XRD-quantitative (*i.e.* Rietveld) and QEMSCAN®. As a conclusion, it was possible to discuss the advantages and limitations of both methods, for the choice of the best routine during feasibility study. Three nonsulfide zinc deposit with different grades of mineralogical complexity have been considered for this purpose: Hakkari Zn(Pb) in Turkey; Jabali Zn-Pb(Ag) in Yemen; Reef Ridge Zn in Alaska. The general geology, mineralogy and geochemistry of each of these deposits have been evaluated separately, either from already known reference literature, or on the base of recently obtained scientific results. These data are considered preliminary to the QEMSCAN® analyses, and should be assimilated during the evaluation through Automated Mineralogy.

The Hakkari deposit (Turkey)

The Hakkari zinc deposit is located in the extreme southeastern region of Turkey (Fig. 1a), approximately 10 km west of the town of Hakkari, within a broad 20 km wide and 100 km long east-west belt. The orebodies, consisting of both sulfide and nonsulfide Zn ≫ Pb ores occur in Middle-Triassic to Early Cretaceous shallow water carbonate rocks within the northern margin of the Arabian Platform (Grodner, 2010). The nonsulfide ore, which represent the most economic portion of the deposit consists of overall estimated compliant resources of at least 10 Mt @ 15% Zn (MSA Group Ltd., 2013.).

Traditional techniques were used to carry out a complete geochemical, petrographic and mineralogical characterization of the Hakkari economic concentrations. The mineral association typically comprises smithsonite and hemimorphite (Santoro *et al.*, 2013), which apparently replace both sulfide minerals and carbonate host rock. Two generations of smithsonite occur: the first is relatively massive, the second occurs as concretions in cavities. Some zinc is also hosted within Fe-Mn-(hydr)oxides. Lead is present in cerussite, but also in Mn-(hydr)oxides. In the whole mineralized area, a diffuse As-Sb-Tl geochemical enrichment also occurs

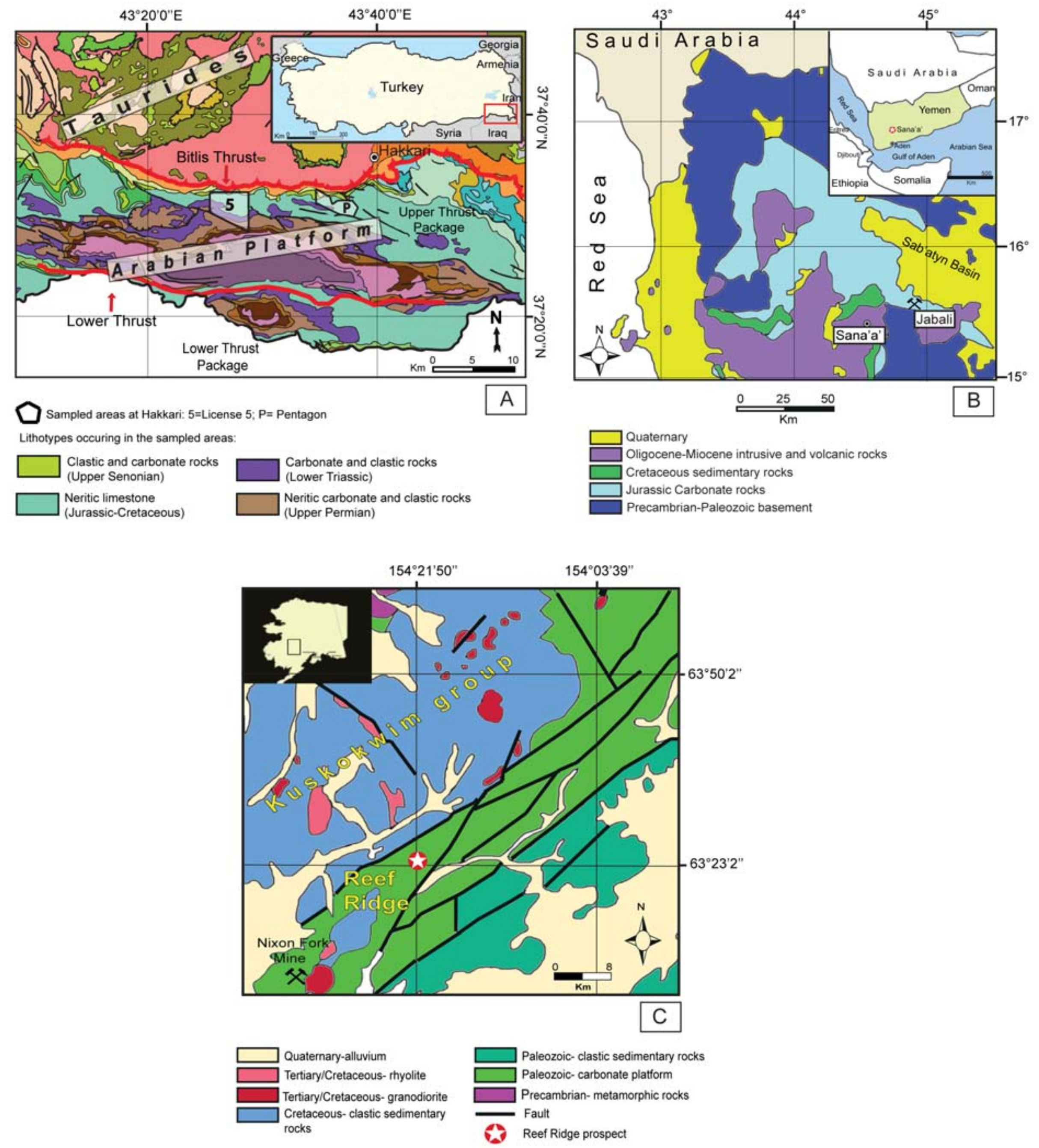

Fig. 1 - a) Geological sketch map of the Hakkari area with the location of License 5 and Pentagon, where the sampling has been carried out (Santoro *et al*., 2013); b) Geological map of western Yemen, with the location of the Jabali deposit (Santoro *et al*., 2015a); c) Geologic map of the Upper Kuskokwim area (from Santoro *et al*., 2015b) showing Reef Ridge and other Zn prospects.

and silver is also present locally (Santoro *et al.*, 2013). The features of the supergene mineralization suggest that the Hakkari deposit belongs both to the "direct replacement" and "wall rock replacement" after the Hitzman *et al.* (2003) classification.

The Hakkari samples were analyzed quantitatively both by the XRD-Rietveld and QEMSCAN® methods. QEMSCAN® analysis also allowed a more detailed mineralogical characterization of several Hakkari drill cores. The study with the "Automated Mineralogy" technique confirmed the main mineral phases (smithsonite and hemimorphite) recorded with traditional methods, but identified other phases not previously detected (*e.g.* minerals in trace amounts such as sauconite), being also able to distinguish and quantify impure phases (*e.g.* Zn-dolomite, Cd-calcite), and identify amorphous phases [pyrite/Fe-(hydr)oxides/jarosite mix] that XRD had found challenging (Santoro *et al*., 2014).

In particular, the modal mineralogy of the ore and gangue minerals, the mineral association and the spatial distribution data obtained by the mineral maps (Fig. 2) of the economic minerals at Hakkari provided information for the advanced exploration phase of the deposit.

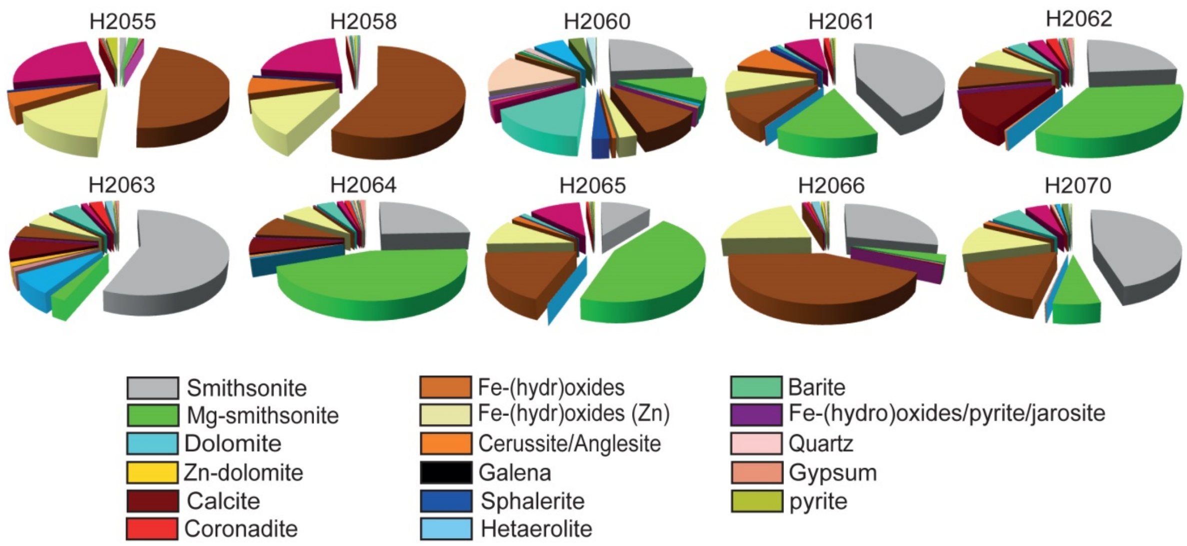

Fig. 2 - QEMSCAN Quantitative analyses of selected core samples from the Hakkari deposit.

The Jabali deposit (Yemen)

Jabali is a Zn-Pb-(Ag) nonsulfide deposit, located 110 km northeast of Sana'a, the capital of Yemen along the western border of the Marib-Al-Jawf/Sab'atayn basin (Fig. 1b). The deposit covers an area of about 2 km^2. The orebody is hosted in the Jurassic carbonate rocks of the Shuqra Fm. (Al Ganad *et al*., 1994). It is almost completely oxidized with only a small portion unaltered, thanks to an impermeable sediment cover. Ore characterization by the use of traditional analytical techniques revealed that smithsonite is the main zinc mineral, while hemimorphite and hydrozincite are less common. Cerussite and anglesite also occur as main lead minerals. Goethite, hematite, and Mn-(hydr)oxides are common throughout the mining area. Ag-sulfides and native silver are also present locally. Zn-enriched dolomite was detected by the use of SEM-EDS in many samples from several zones of deposit, even if not quantified by XRD-Rietveld analyses (Mondillo *et al*., 2014).

Several hypotheses have been formulated on the age and genesis of the supergene mineralization. Some authors proposed a long period of oxidation, subdivided in several phases, extended from Cretaceous to present, whereas others believe that there has been a single oxidation stage, which started in Miocene and continues until present (Al Ganad *et al.*, 1994; Allen, 2000). A renewed mineralogical characterization and quantitative evaluation of the Jabali deposit was carried out by the use of QEMSCAN® automated technology, and proposed as one of the main subjects of this thesis. The main aim was the improvement of the knowledge of the mineral association and element deportment in the Jabali supergene ore. The results (Fig. 3) confirmed the main mineralogical findings of the previous studies, and added new and more detailed information: smithsonite is mostly associated and intergrown with Fe-(hydr)oxides and remnants of primary sulfides. The host dolomite is locally replaced by broad bands of Zn-rich dolomite (which has been quantified by QEMSCAN®), where Zn has substituted for Mg. Hemimorphite, cerussite and anglesite occur in minor amounts. The Ag-sulfides are mainly

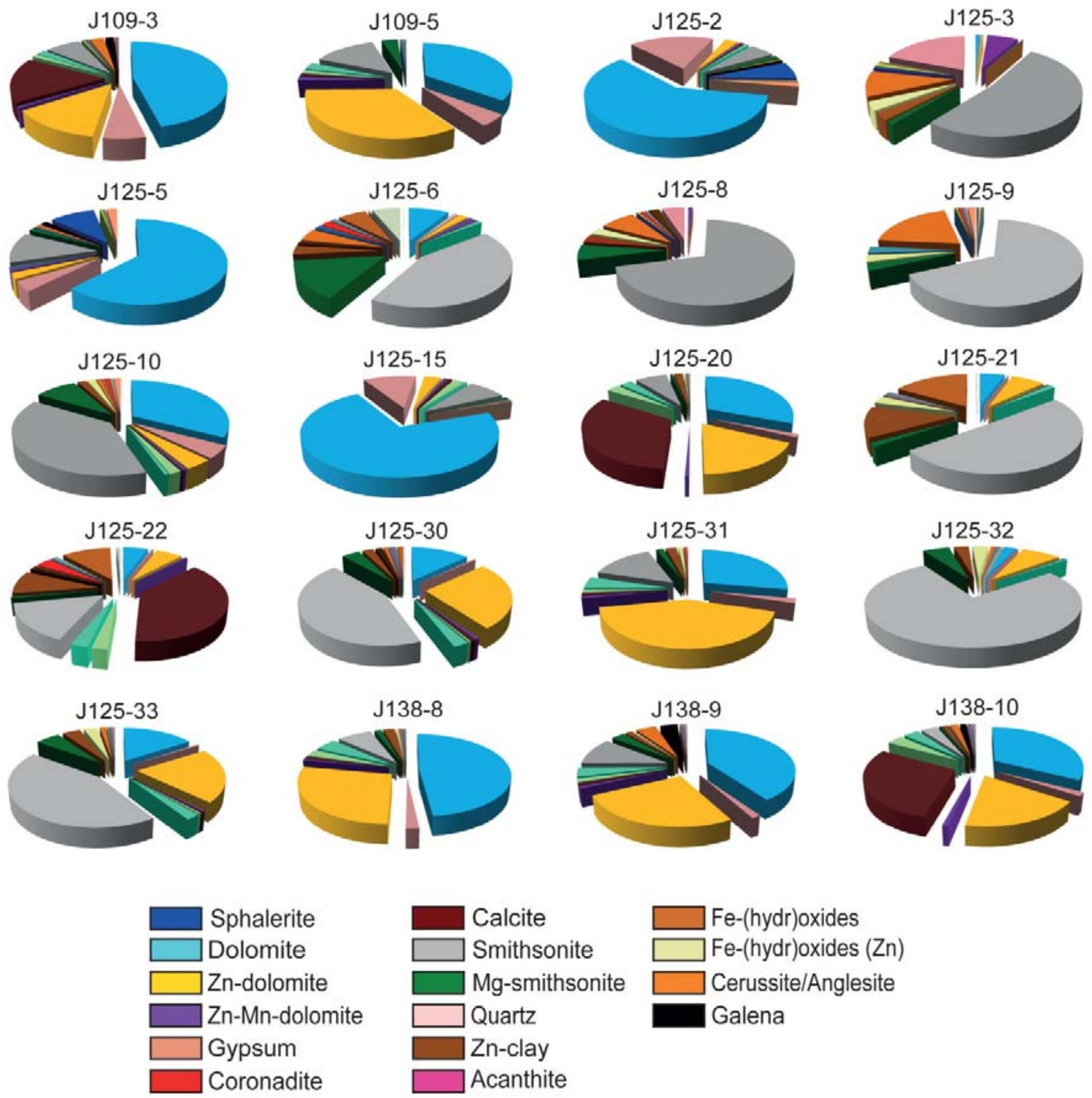

Fig. 3 - QEMSCAN Quantitative analyses of selected core samples from the Jabali deposit.

associated with anglesite. Gypsum, Fe-(hydr)oxides (goethite > hematite), Zn-Mn-(hydr)oxides and Pb-Mn-(hydr)oxides have been detected locally (Santoro *et al*., 2015a).

The QEMSCAN® technique, hence, combined with data previously obtained by other analytical techniques (XRD, SEM-EDS, optical petrography), has provided detailed mineralogical and textural information on the Jabali mineralization. A key outcome from the QEMSCAN® study have been the textural data and quantification of the Zn-dolomite: this was an important result, because the occurrence of abundant Zn-dolomite in the host rock caused issues in the recovery steps during the choice of the best processing route. The combination of techniques used to examine the Jabali supergene ore provided high quality information that not only characterizes the deposit in detail, but also offers a better understanding for the design of ore processing options and a more realistic predicted recovery of economic minerals.

The Reef Ridge Prospect (Alaska)

The Reef Ridge prospect (Fig. 1c) is a typical supergene nonsulfide zinc mineralization, located in the Yukon-Koyukuk region of west central Alaska (USA). It is hosted in sedimentary rocks of the Farewell Terrane (Decker *et al*., 1994), a continental fragment sandwiched between the Siberian and Laurentian cratons during the early Paleozoic. The mineralization occurs in Lower-Middle Devonian dolomites, belonging to a Paleozoic carbonate platform succession and has been considered as MVT in origin. The supergene concentrations consist of oxidized minerals, associated with minor sulfide remnants. As the other two analyzed deposits, also Reef Ridge shows the features of both "direct replacement" and "wall rock replacement" supergene ores.

The results of a complete petrographic and mineralogical study (XRD, chemical analysis, SEM-EDS and QEMSCAN®) show that Reef Ridge has a simple mineralogy compared to the Hakkari and Jabali deposits. The most abundant mineral in the nonsulfide ore assemblage is smithsonite (Fig. 4). Similarly to other nonsulfide zinc deposits worldwide, a first generation of smithsonite has replaced both primary sphalerite and the host carbonates. A second smithsonite generation precipitated as cement in vugs and fractures. Minor zinc amounts also occur in the Fe-(hydr)oxides and zinc traces have been identified in clay minerals (Santoro *et al*., 2015a).

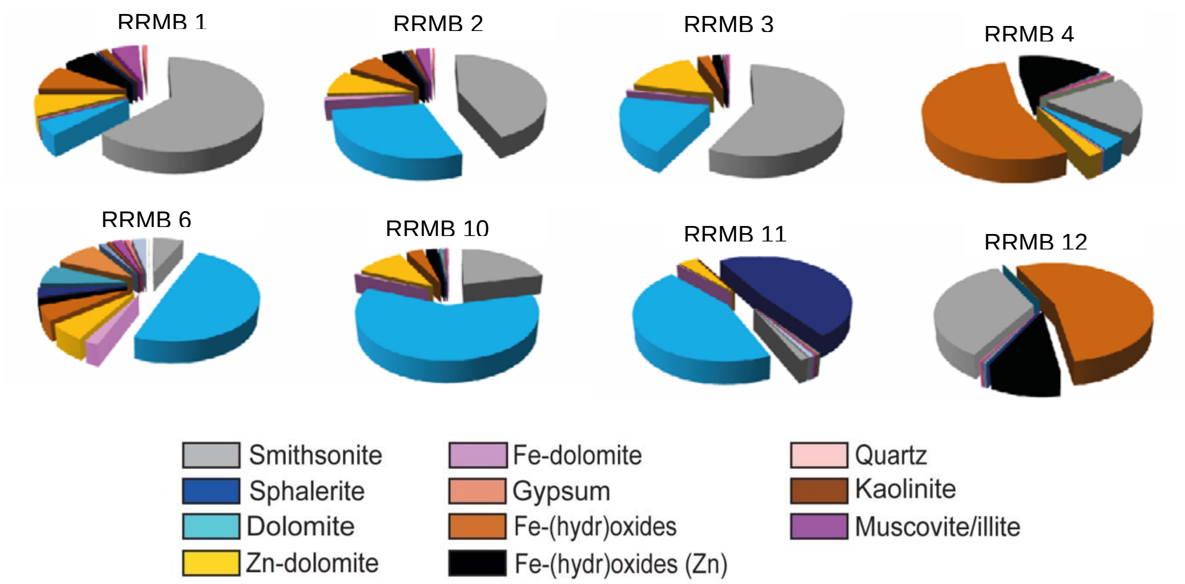

Fig. 4 - QEMSCAN Quantitative analyses of Reef Ridge selected core samples.

Geochemical isotope analyses have been carried out on the carbonate minerals, in order to define the genesis of the supergene ore (Santoro *et al*., 2015b). The carbon and oxygen isotope values of smithsonite at Reef Ridge range from -0.7 to 2.1‰ VPDB and 19.1 to 21.9‰ VSMOW, respectively. The $\delta^{13}C$ values suggest that the predominant carbon source for smithsonite were the host carbonates, with a limited contribution from organic carbon. The oxygen isotope ratios are much more depleted in ^{18}O compared to supergene nonsulfides from other parts of the world, formed under warm-humid, temperate or semi-arid climates (Gilg *et al*., 2008). The depletion in ^{18}O of precipitating waters indicate that the formation of the Reef Ridge nonsulfide deposit was probably related to cold/humid weathering episodes during late Tertiary to Recent (Santoro *et al*., 2015a). These findings have subverted the "traditional" theory that the supergene Zn nonsulfide deposits only form in warm-humid, temperate or semi-arid conditions.

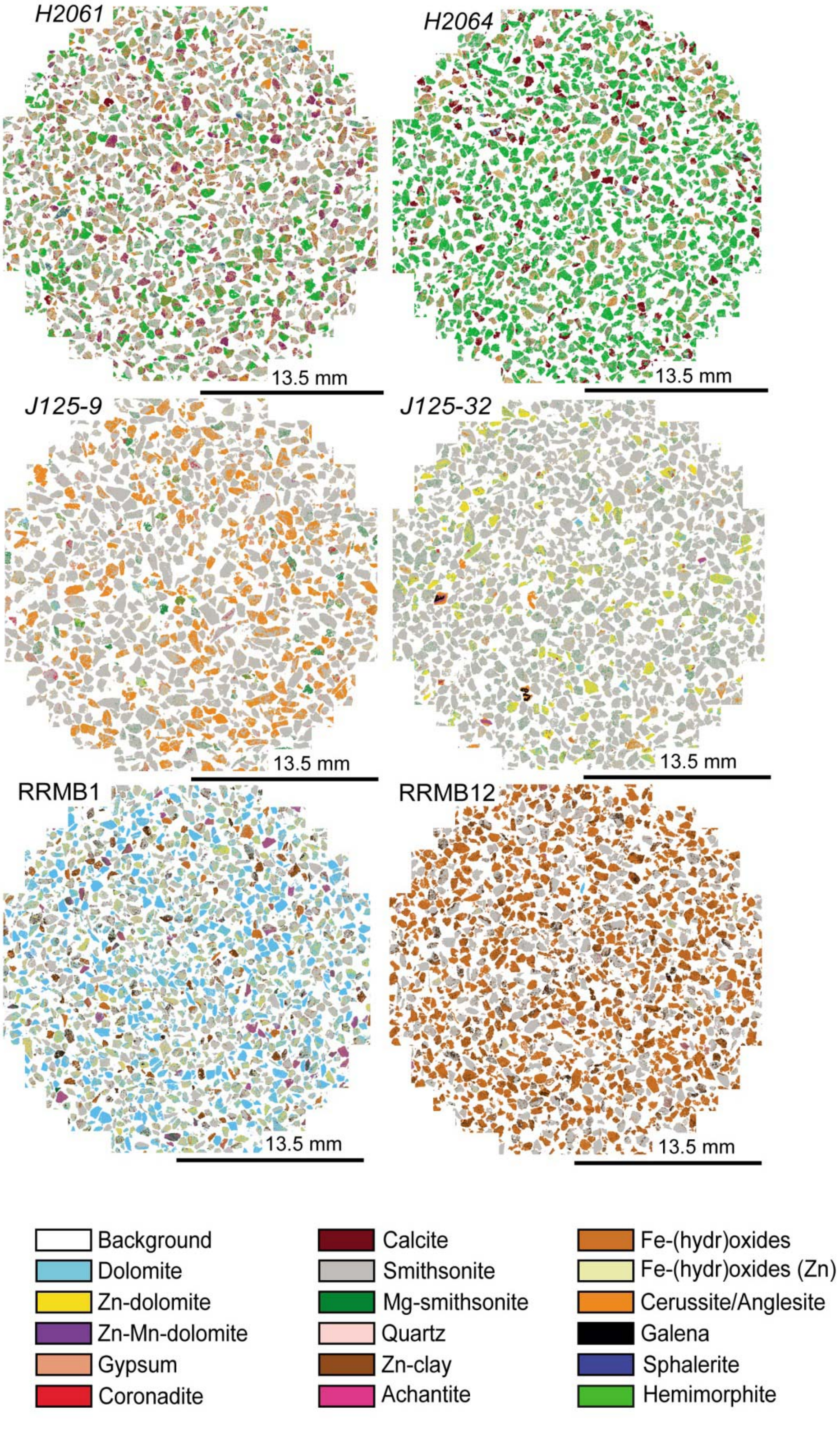

Fig. 5 - QEMSCAN Quantitative analyses of selected core samples analyzed by QEMSCAN® (false-color fieldscan images). Samples H2061 and H2064 from the Hakkari deposit; samples J125-9 and J125-32 from the Jabali deposit; samples RRMB1 and RRMB12 from the Reef Ridge prospect (Santoro *et al*., 2014, 2015a, 2015b).

DISCUSSION AND CONCLUSIONS

Although the considered deposits represent three typical examples of supergene nonsulfide Zn-(Pb) ore concentrations, their study has revealed several important mineralogical and petrographic differences: Jabali resulted to be the most mineralogically complex of the three, due to the number of occurring mineral phases (smithsonite, Fe-(hydr)oxides, cerussite, anglesite, remnants of sphalerite and galena, and several other minor phases, *i.e.* Ag-minerals, sauconite, kaolinite, gypsum, calcite) and because of the local occurrence of high amounts of Zn-(Pb) in several mineral phases (*i.e.* Zn-dolomite). The mineralogy of the Hakkari deposit is also not straightforward, with zinc occurring mainly as smithsonite and hemimorphite, lead as cerussite and anglesite, associated with Fe- and Mn-(hydr)oxides. The mineralogy of the Alaskan deposit, instead, is quite simple, because it consists of smithsonite, with some Fe-(hydr)oxides and rare sphalerite.

The study of these three deposits was carried out with the use of several traditional techniques, and a more recent analytical technique (QEMSCAN®) to better comprehend the characteristics of the deposits. During the analyses I was faced with several issues that sometimes resulted in inaccurate information and misleading data: *e.g.* the occurrence of unidentified amorphous phases, the effective absence of phases wrongly determined earlier (*i.e.* ankerite and Zn-ankerite), the occurrence of not quantificable mixed phases, and the difficulty to characterize a few mixed mineral compounds. To overcome these problems, it was necessary the support of several analytical techniques, and the comparison of the results obtained with each of them.

The main conclusion of this study is that the characterization of nonsulfide Zn-deposits, and especially their quantitative evaluation (QPA) may be quite tricky, because of their complex mineralogy. The lack of accurate mineralogical results can cause several problems in the processing and metallurgical stages (recovery issues, penalties at the smelter, poor metal quality, and environmental damage).

QEMSCAN® is an useful tool for ore characterization during exploration and potential processing steps nonsulfide deposits, as it can provide mineral maps (Fig. 5) furnishing detailed information on the texture, add significant information on the major and trace mineral distribution, and produce a good quantitative evaluation of the isomorphic phases that typically characterize the minerals occurring in this kind of deposits. However, even though there are many positive aspects in applying this technique, it is important to remark that the QEMSCAN® data cannot be used alone, because of the mentioned ambiguity in minerals identification.

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