

AQUAMARINE FROM THE MASINO-BREGAGLIA MASSIF, CENTRAL ALPS, ITALY

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Aquamarine from granitic pegmatites of the Masino-Bregaglia Massif, Central Alps, Italy, is investigated by classical gemological methods, LA-ICP-MS chemical analyses, and UV-Vis-NIR and mid-IR spectroscopy. This beryl has typical gemological properties for aquamarine, including iron absorption features, and is characterized by a low alkali content and both types I and II water molecules. Although so far only a small amount of this aquamarine has been polished into gems, it represents an attractive gem material of potential economic interest.

The Masino-Bregaglia Massif (also known as the Bergell Massif) contains numerous granitic pegmatites hosting a remarkable variety of minerals—including aquamarine (figure 1)—that have attracted the interest of mineralogists and collectors since the late 18th century (e.g., Bedogné et al., 1995). Beryl from this area was initially mentioned by Repossi (1916) and Staub (1924). Subsequently, many other beryl occurrences were discovered in the massif. In their listing of the locations of historical beryl-bearing pegmatites, Hügi and Röwe (1970) indicated that the most important Italian deposits occurred in the areas of Val Bregaglia (Bregaglia Valley), Valle Mello, Cima di Zocca, Val Masino, Val Codera, and Alpe Vazzeda. In the 1970s, a limited amount of gem-quality aquamarine was recovered and cut from the Filone Silvana (Silvana dike), located in Val Codera.

Masino-Bregaglia aquamarine crystals typically show a prismatic habit and measure several centimeters long, although some crystals attain ~15–20 cm in length. They range from light to dark greenish blue to blue or yellow-green. Some gem- and carving-quality aquamarine has

been recovered, although the fact that most of the crystals contain numerous inclusions and fractures makes such material rare (Bedogné et al., 1995).

To our knowledge, a gemological characterization of this aquamarine is lacking, except for the recent work of Caucia et al. (2008, in Italian). The present article builds on that work by supplying additional data obtained on a larger number of samples from four pegmatites in this area.

Geologic Setting. Masino-Bregaglia is a composite pluton located at the border of Italy and Switzerland (figure 2). It consists mainly of a medium-grained tonalite at the margin and a coarse-grained granodiorite in the core (Trommsdorff and Nievergelt, 1983), which crystallized 32 and 30 million years ago, respectively (von Blanckenburg, 1992). Younger cross-cutting granitic pegmatites and aplites are found throughout the pluton, and some of the pegmatites contain beryl, garnet, tourmaline, and a suite of rare minerals (Wenger and Armbruster, 1991; Bedogné et al., 1995).

Figure 1. This 2.33 ct aquamarine is from the Masino-Bregaglia Massif, Italy. Courtesy of Francesco Bedogné; photo by Roberto Appiani.



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Materials and Methods. We examined 14 aquamarine samples from the Masino-Bregaglia Massif: five cabochons (0.30–5.79 ct) and three crystals (4.8–12.0 g, obtained from three different rough specimens) from Val Codera (e.g., figure 3); one faceted (0.26 ct) and one rough (9.6 g) sample from Cima di Zocca; one faceted (0.90 ct) and one unpolished sample (4.0 g) from Val Bregaglia; and one faceted (2.44 ct) and one rough (8.7 g) sample from Alpe Vazzeda. The studied samples are in the collection of the Earth Sciences Department Museum of the University of Milan.

All cut samples were examined by standard gemological methods to determine their optical properties, hydrostatic specific gravity, UV fluorescence, and microscopic features.

Chemical analyses were performed on the six rough specimens by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS), using an Elan DRC-e mass spectrometer coupled with a Q-switched Nd:YAG laser source, with a fundamental emission (1064 nm) that was converted to 266 nm by two harmonic generators. Helium was used as a carrier gas, mixed with Ar gas downstream of the ablation cell. The calibration was performed using NIST SRM 610 glass and Si as external and internal standards, respectively. The precision and accuracy estimated on the basaltic glass BCR2 standard were better than 10%. Four analyses per sample were collected using a spot size of 40 μm .

Nonpolarized UV-Vis-NIR spectra of three aquamarines (two crystals from Val Codera and one faceted gem from Val Bregaglia) were collected with a Lambda 950 PerkinElmer spectrometer, equipped with an integrating sphere, over the 250–1300 nm range.

Mid-infrared (4000–400 cm^{-1}) spectra of the six rough samples were collected in transmission mode by a Nicolet Nexus FTIR spectrometer, with a resolution of 4 cm^{-1} , using KBr pellets consisting of 2 mg of powdered sample mixed with 200 mg KBr.

Results and Discussion. The cut stones ranged from light to medium blue to greenish blue, and were transparent to opaque. Gemological testing gave the following properties: $\text{RI}-n_o = 1.580\text{--}1.590$ and $n_e = 1.572\text{--}1.579$, birefringence—0.008–0.009, optic character—uniaxial negative, $\text{SG}-2.67\text{--}2.72$, and inert to both long- and short-wave UV radiation. These observations are consistent with those reported in the literature for aquamarine (O'Donoghue, 2006). The samples were fairly heavily included; they contained fractures, partially healed fissures with fluid and two-phase (fluid and gas) inclusions (figure 4), and growth lines.

LA-ICP-MS measurements (table 1) showed a distinct amount of the chromophore Fe (0.46–0.74 wt.%), as is present in all aquamarines (see, e.g., Adamo et al., 2008, and references therein). Other possible coloring elements (Ti, V, Cr, Mn) were present at very low trace levels ($<<0.1$ wt.%), as were the alkaline earth metals (Ca and Mg) and the alka-

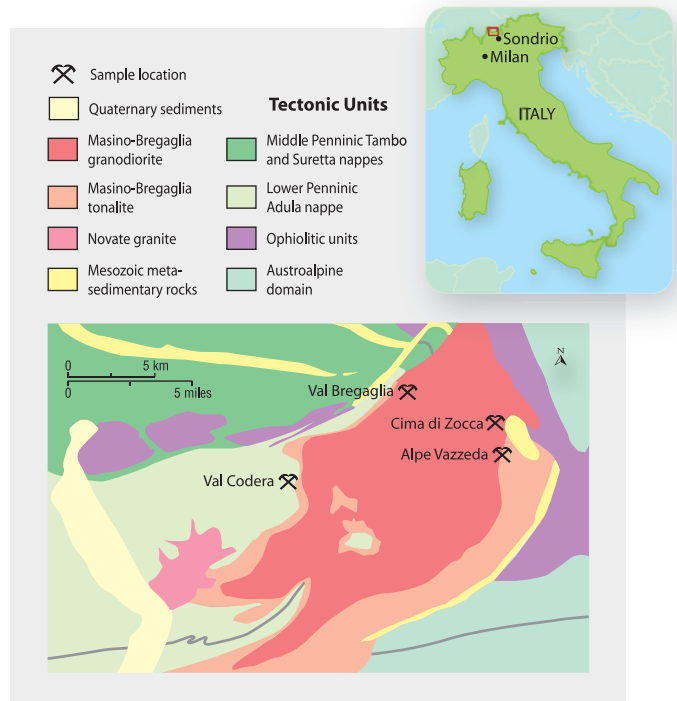


Figure 2. This simplified geologic map illustrates the composite pluton of the Masino-Bregaglia Massif, Central Alps, Italy, and the locations of four of the granitic pegmatites where the beryl samples studied were found.

li metals (Li, Rb, Cs). The only exception was Na, which ranged from 0.22 to 0.39 wt.%. On the basis of these data, our samples can be considered low-alkali-bearing beryls, per the classification of Schmetzer and Kiefert (1990).

Figure 3. These aquamarine crystals (~3.5–4 cm long) from Italy's Val Codera pegmatite were among those investigated in the present study. Photo by R. Bocchio.



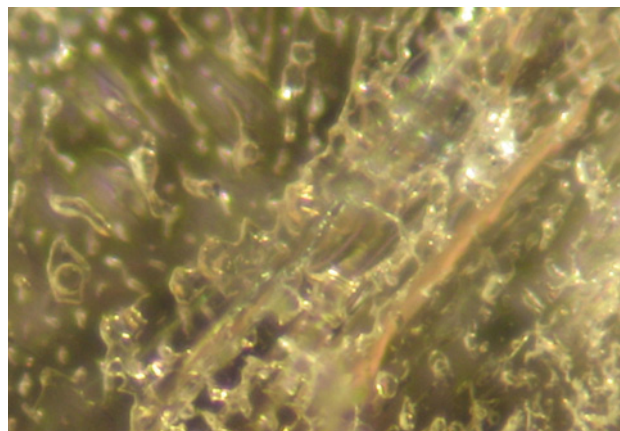


Figure 4. Fluid inclusions (some containing a gas bubble) are common features in aquamarine from the Masino-Bregaglia Massif (here, from Val Codera). Photomicrograph by I. Adamo; magnified 45 \times . The brown color is an artifact of the lighting conditions.

The UV-Vis-NIR spectra were typical for aquamarine (e.g., figure 5, top), with a general absorption below ~ 300 nm, two peaks at 370 and 426 nm related to Fe^{3+} , and a strong and broad absorption band centered at about 820 nm that was due to Fe^{2+} (Wood and Nassau, 1968; Burns, 1993; Taran and Rossman, 2001; Spinolo et al., 2007). A sideband at about 600 nm has been attributed to an Fe^{2+} - Fe^{3+} intervalence charge-transfer process (Schmetzer, 1990; Burns, 1993; Taran and Rossman, 2001), although some authors (e.g., Wood and Nassau, 1968; Viana et al., 2002) have assigned it to Fe^{2+} .

The mid-infrared spectra (e.g., figure 5, bottom) contained absorption bands below 1200 cm^{-1} intrinsic to the beryl structure, as well as features originating from both type I (3699 cm^{-1}) and type II (~ 3660 and 3597 cm^{-1}) water

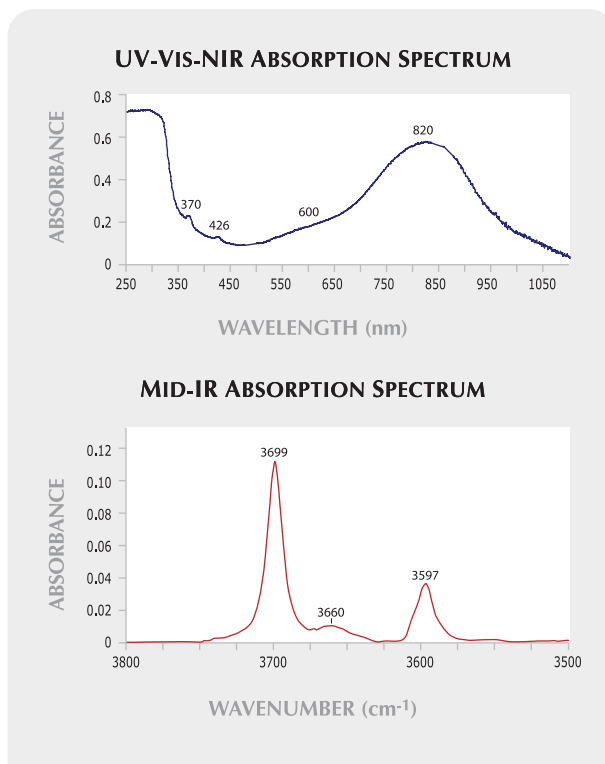


Figure 5. As is typical for aquamarine, this UV-Vis-NIR spectrum (top) of the faceted specimen from Val Bregaglia is characterized by absorption features related to iron, which is responsible for the blue color. The representative mid-IR spectrum in transmission mode (bottom) shows the region of water-stretching vibrations ($3800\text{--}3500\text{ cm}^{-1}$) and is characterized by absorption features of water molecules in both type I (at 3699 cm^{-1}) and type II (at ~ 3660 and 3597 cm^{-1}) configurations in the structural channels.

TABLE 1. Average LA-ICP-MS analyses of six aquamarine samples from the Masino-Bregaglia Massif, Central Alps, Italy.

Minor and trace elements (ppm)	Val Codera			Cima di Zocca	Val Bregaglia	Alpe Vazzeda
	1	2	3			
Li	58	62	126	267	275	116
Na	2187	2625	2500	3930	3838	2939
Mg	644	638	579	1067	1033	411
Ca	310	245	155	176	176	123
Ti	29	30	40	56	52	57
V	1.6	1.7	2.5	0.40	0.92	0.80
Cr	5.7	4.0	1.6	1.60	1.68	1.40
Mn	50	48	88	91	85	158
Fe	4666	4633	7273	6361	6280	7444
Zn	543	535	317	381	375	177
Rb	34	34	92	46	47	49
Cs	661	662	613	729	735	1228

molecules trapped in the structural channels (Wood and Nassau, 1967, 1968; Charoy et al., 1996; Fukuda and Shinoda, 2008). In agreement with the chemical composition, the IR spectrum is typical of low-alkali-bearing beryl, both natural and synthetic (Schmetzer and Kiefert, 1990; Adamo et al., 2008).

Conclusions. Aquamarine from the Masino-Bregaglia Massif shows typical gemological properties. The studied specimens consist of low-alkali-bearing beryl that contains water molecules in both type I and II configurations. Iron is the chromophore, as is typical for aquamarine. This area is one of the most significant localities for gem-quality aquamarine in Italy, although fine material has been found only in limited amounts and only a few pieces have been set into jewelry (e.g., figure 6). Local mineral collectors continue to work the deposits, and it is likely that small amounts of gem-quality aquamarine will continue to be produced in the future.



Figure 6. This 8.5 ct aquamarine cabochon from the Masino-Bregaglia Massif is set with diamonds. Photo by, and specimen courtesy of, Pietro Nana.

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